

# FABRICATION OF AN OXYGEN SENSOR AND ITS APPLICATION TO INVESTIGATE IRON ORE-CARBON REACTION

By

AVINASH KESHAV GOKHALE

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DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
AUGUST, 1975

# **FABRICATION OF AN OXYGEN SENSOR AND ITS APPLICATION TO INVESTIGATE IRON ORE-CARBON REACTION**

**A Thesis Submitted  
in partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY**

**By  
AVINASH KESHAV GOKHALE**

**to the**

**DEPARTMENT OF METALLURGICAL ENGINEERING  
INDIAN INSTITUTE OF TECHNOLOGY KANPUR  
AUGUST, 1975**



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## CERTIFICATE

Certified that this work on "Fabrication of oxygen sensor using solid electrolyte technique and its application for the investigation of the iron ore-carbon reaction" has been carried out under my supervision and that it has not been submitted elsewhere for a degree.

A. Ghosh

Professor  
Department of Metallurgical Engineering  
Indian Institute of Technology  
Kanpur-208016, U.P.

POST GRADUATE OFFICE  
This thesis has been approved  
for the award of the Degree of  
Master of Technology (M.Tech.)  
in accordance with the  
regulations of the Indian  
Institute of Technology Kanpur  
Dated: 26.8.75 24

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## CHAPTER I

### INTRODUCTION AND LITERATURE REVIEW

#### **A) Objective of the work:**

Oxygen sensor based on solid electrolyte cell is a versatile device in measuring and monitoring the oxygen concentration in gases or liquids. The response of the sensor to the change in oxygen concentration is very quick (less than 1 sec.) and the range over which it can be used is very wide. This sensor can be employed for chemical analysis of some gas mixtures as well. Due to these outstanding advantages, the use of this sensor on the commercial scale for various applications is coming up fast in the industrially advanced countries. Since this has not become a common feature in India, it was planned to fabricate an oxygen sensor for gases only, to test <sub>hh</sub> its performance and to use it for laboratory investigations.

The reaction between iron ore and graphite is an important reaction in blast furnace and also in the rotary kiln process of sponge iron making, which offers an important alternative method for iron production. The course of such a reaction can, in principle, be followed by measuring the rates of generation of CO and  $\text{CO}_2$ . The latter could be determined by monitoring the flow-rate of the gas mixture coming out of the reaction chamber and analysing its  $\text{O}_2/\text{CO}_2$  ratio by the solid electrolyte oxygen sensor. Therefore it was chosen for investigation.

#### **B) Literature Review:**

##### **B-1) Solid Electrolyte Oxygen Sensors:**

The review shall be restricted to sensors to be employed

for gases.

Solid electrolytes are solids which allow ionic conduction only. For the oxygen sensor the materials which conduct oxygen ions are of interest. Again the ionic conduction should be very close to 100 pct. if it has to be useful as an electrolyte in a galvanic cell. For this  $ZrO_2 - CaO$ ,  $ZrO_2 - MgO$ ,  $ZrO_2 - Y_2O_3$ ,  $ThO_2 - Y_2O_3$  have been employed. But calcia stabilized zirconia,  $ZrO_2 - CaO$  (CSZ in abbreviation) is the most important one.

A number of review articles have already appeared in the literature (1-4). Therefore the following discussion would be brief.

### B- 1-1 ) Principle of operation of oxygen sensor:

Using the CSZ, an oxygen concentration cell is formed as shown below.

Pt, gas sample		CSZ		reference gas, Pt		1-1
$p_{O_2}$ , $\mu_{O_2}$		( $O^{2-}$ )		$p_{O_2}^0$ , $\mu_{O_2}$		

$$\text{For this cell } E = \frac{-\Delta \theta^0}{2F}$$

$$\therefore E = \frac{RT}{4F} \ln \frac{p_{O_2}^0}{p_{O_2}} \quad (1-1)$$

$$= \frac{1}{20,160} \log \frac{p_{O_2}^0}{p_{O_2}}$$

where  $E$  = emf in millivolts

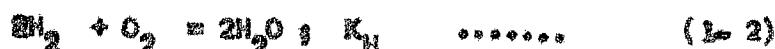
$T$  = Temperature in  $^{\circ}\text{K}$ .

$F$  = Faraday constant

$R$  = Universal gas constant

$P_{O_2}$  is determined from measurement of E and T since  $P_{O_2}^0$  is known.

If the gas contains, besides oxygen and inert gas, any species reactive to oxygen such as  $H_2$  or  $CO$ , then an equilibrium similar to the following prevails, since solid electrolyte cells are operated at high temperatures only



$$\text{and } P_{O_2} = \frac{1}{K_H} \left( \frac{P_{H_2}^0}{P_{H_2}} \right)^2, \quad (1-3)$$

where  $K_H$  is the equilibrium constant of reaction (1-2).

Therefore measurement of  $P_{O_2}$  allows determination of  $P_{H_2}^0/P_{H_2}$  ratio in a gas since the value of  $K_H$  can be calculated from the known standard free energy of formation of  $H_2O$ .

Similarly if the gas contains  $CO$  and  $CO_2$ ,  $P_{CO}/P_{CO_2}$  ratio can be determined. Knowing the total pressure,  $P_{CO}$  and  $P_{CO_2}$  can be calculated individually.

The above examples illustrate as to how the oxygen sensor may be employed for gas analysis.

Over years many methods are being used for oxygen analysis in gases such as Great apparatus, spectrometry, gas chromatography etc. But the discovery of the concentration cell using solid electrolyte has led to a very successful breakthrough in oxygen concentration measurement in various phases. The outstanding advantages are:

1. If response is specific, rapid and continuous.
2. If measurement can be done without disturbing the system.
3. Single sensor can be used over wide ranges of oxygen content.

and temperature.

4. The cell voltage is amenable to high precision measurement.
5. It can be used for the system not containing oxygen also since it measures oxidizing potential as such.
6. CSZ is excellent ceramic material and stands high temperatures.

There are some inherent limitations also

- 1) It can not be used below 800°C because of high resistance and also irreversibility.
- 2) It has a poor thermal shock resistance.

#### B-1-II Some basic considerations

Since both the electrodes are gases, there is a need to separate them completely. It can be done in two ways as shown in figure 1-1. Generally platinum is used as lead wires. It is suitable because of its low reactivity and high melting point. Its surface quickly attains equilibrium with respect to gaseous phase. Ni, In, Au etc can be used but are costlier.

#### B-1-III Leakage of oxygen:

One problem with solid electrolyte is the leakage of oxygen from reference to the sample gas side (or vice versa) through pores or due to electronic conduction in solid electrolyte. The latter is the predominant mechanism of leakage (3), and it increases sharply with temperature.

When oxygen concentration in inert gas oxygen mixture is measured, especially at low oxygen concentrations, this leakage of oxygen may lead to considerable error in measurement. So to keep the

error within limit, one has to increase the flow of the gas mixture in order/make the influence of leaked oxygen negligible.

If there is a leak of  $4 \times 10^{-5}$  cc/sec. at  $1200^{\circ}\text{K}$ , with pure oxygen as reference, in order to cut down the error to less than 4% the flow rates of the  $\text{Ar}-\text{O}_2$  mixture should be at least 0.1, 10,  $10^3$  cc/sec. for  $P_{\text{O}_2}$  values of  $10^{-2}$ ,  $10^{-4}$  and  $10^{-6}$  atmospheres respectively. This means that reasonably accurate measurement is possible upto  $P_{\text{O}_2} \simeq 10^{-4}$  atmospheres only (5).

Instead of inert gas oxygen mixture if  $\text{CO}-\text{CO}_2$  or  $\text{H}_2-\text{H}_2\text{O}$  mixture is present, then the buffering capacity of the gas is considerably enhanced. The leaked oxygen reacts with  $\text{H}_2$  or CO forming  $\text{H}_2\text{O}$  and  $\text{CO}_2$  respectively. Since the change in the concentration of  $\text{CO}_2$  or  $\text{H}_2\text{O}$  is very small, it does not change the  $\text{CO}/\text{CO}_2$  or  $\text{H}_2/\text{H}_2\text{O}$  ratio appreciably so even for very low oxidizing potentials reasonably low flow-rates may be employed.

#### B-I-IV Operating temperature range:

At low temperature, resistivity of the electrolyte is high and irreversibility sets in the electrode reaction. Moreover the contact between the Pt-electrode and the solid electrolyte becomes poor. The minimum operating temperature is held to be  $600^{\circ}\text{C}$  by various investigators.

At high temperature, leakage rates are highly enhanced, electronic conduction increases and volatilization of platinum as oxide begins. The construction and maintenance of the assembly also becomes difficult. The upper temperature reported so far is  $1300^{\circ}\text{--}1500^{\circ}\text{C}$ .

### B-I-V Measurement of the cell emf:

The emf  $E$  in the equation (I-1) is the open circuit emf in ideal case. So no current should be drawn while measuring the cell emf. Otherwise the reading may be considerably erroneous. So measurement is done with high impedance voltmeter. The minimum input impedance is about one megohm.

### B-I-VI Industrial applications:

Two approaches are possible regarding the use of oxygen sensor. It may be directly introduced into the reaction tube or furnace and direct measurement be made. Alternatively, it may be kept as separate instrument with its own heating arrangement. Latter is preferable since it increases the life of the sensor because of absence of thermal shocks, mechanical and chemical damage etc. Moreover it increases the accuracy since its design can be made sophisticated.

So far this kind of meter is primarily being put to monitor and control the gas composition than to make accurate measurements. It is being used in combustion control, basic oxygen furnace, annealing of metal products, analysis of flue gases in blast furnace, the generation and control of carburizing atmosphere etc.

Few commercial designs have also come up, some of which are the followings.

#### 1) Westinghouse oxygen analyzer (6)

Some of its applications are

- a) Measurement of oxygen impurities in high purity gases.
- b) Chemical plants: Inert gas blanketing control. Control and measurement of oxygen concentration in feed streams.

c) Food Industry: Inert gas blanket monitoring over vats, processing vessels and for industrial safety.

2) Use of oxygen sensor in combustion control of the furnace (7)

It senses the oxygen concentration in the furnace flue gases and provides a corrective signal for furnace combustion control.

3) Pulmonary function oxygen monitor<sup>(8)</sup>.

This is for the medical applications. It provides a direct read out of the oxygen concentration in each inspiration-expiration cycle. The oxygen concentration is accurately recorded ( $\pm 1\%$ ) on a moving strip chart which even depicts a variation caused by the heart beat during expiration. Its typical applications are:

- a) Continuous monitoring of post cardiac surgery patient
- b) respiratory efficiency in the post-operative patient
- c) Study of the cardiovascular system through the effect of exercise upon respiration.

### 3.2 Reduction of Iron Ore by Carbon:

It was recognized even in early days, that kinetically, a solid-solid reaction is expected to be much slower compared to a gas-solid one since solid-solid contact area is much smaller compared to gas-solid contact area and solid-state diffusion is much slower compared to mass transfer in gaseous.

Several investigators (9,10,11) attempted to measure the rates of direct reduction by continuous evacuation of the chamber in the temperature range of  $700-1100^{\circ}\text{C}$  and pressure range of  $5 \times 10^{-4}$ -

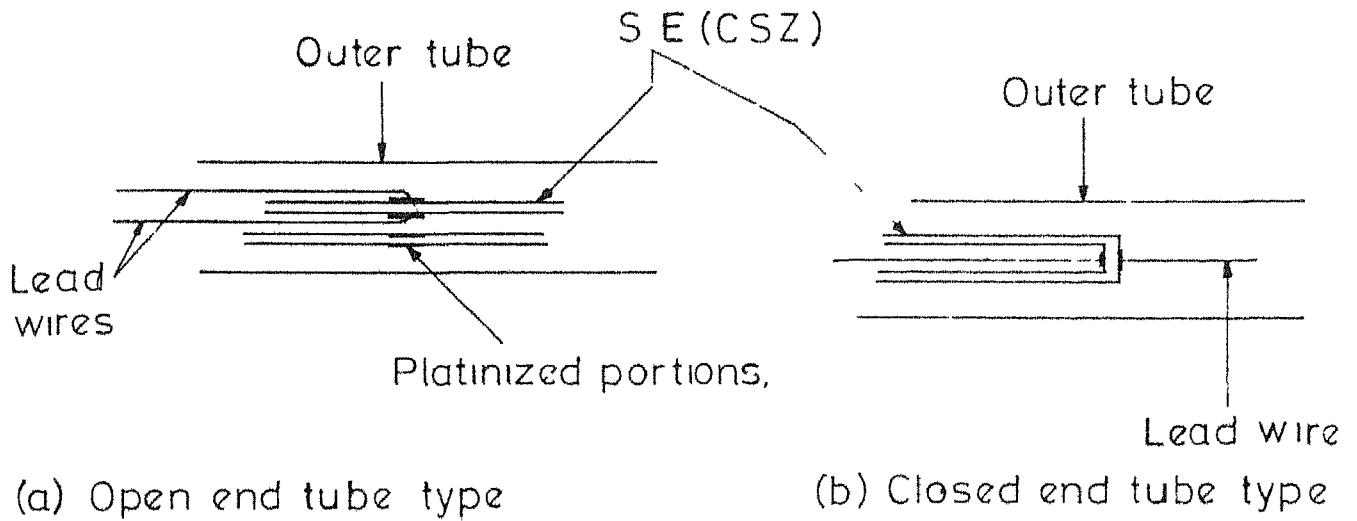


FIG 11

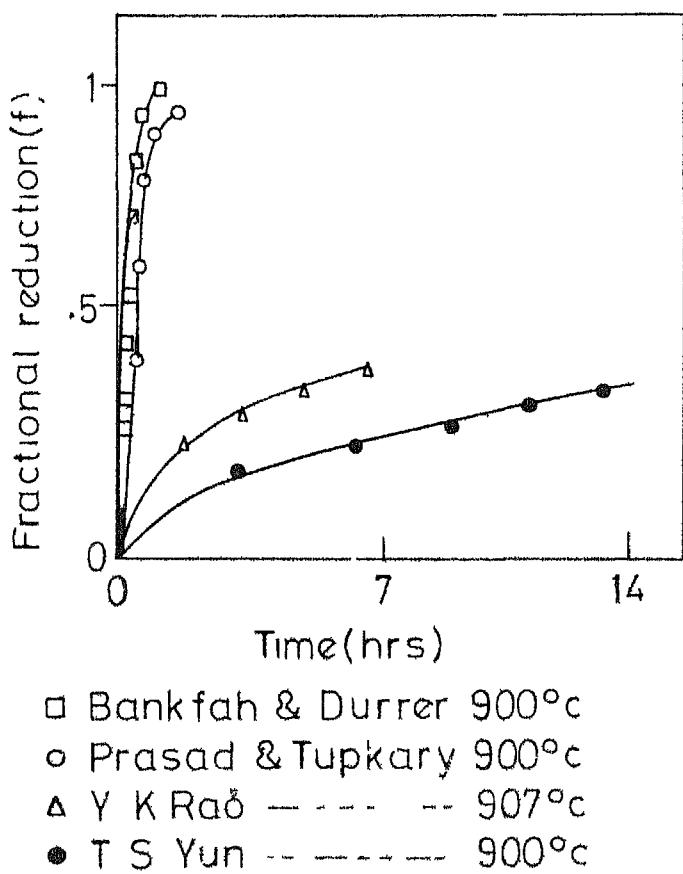


FIG 12

$10 \times 10^{-4}$  torr. They assumed that the gas phases were substantially eliminated by evacuation and hence reaction rates obtained represented those of solid-solid reaction. These results were compared (12) with the experimental data obtained by Y.K. Rao (13), who employed inert gas flushing and that of Baldwin (14), who passed nitrogen over the heated bed of iron oxide and coke.

Results are shown in fig. (1-2). It may be seen that the rates under inert gas flushing were even smaller compared to those obtained under evacuated conditions. These discrepancies were explained by Abraha and Ghosh (12) in the following way. Flow of gas through a pore is 'Knudsen' when the mean free path is larger than the pore diameter. This condition is very well met in the tiny pores of pellets under the reduced pressure. So although the chamber was evacuated the pressure inside the fine pores of the pellet were likely to be appreciable, because flow of CO and  $\text{CO}_2$  from the interior of the pellet to the chamber would require a substantial pressure.

Reduction of iron oxides by carbon occurs in the following two stages.

Reduction of the oxide viz.



and gasification of carbon, viz



First of all the salient kinetic features of these two stages will be presented.

### 3-2-1 Kinetics of reduction of iron oxides by carbon monoxide

Some investigators studied the reduction kinetics of  $\text{Fe}_2\text{O}_3$ . Both single-pellet cum thermobalance technique (15, 16) as well as packed bed systems were employed (17, 18, 19). The temperature ranged from  $700^\circ\text{C}$  to  $1200^\circ\text{C}$  and both CO as well as mixtures of CO and  $\text{CO}_2$  were employed. The particle size ranged from a fraction of a millimeter to 4 centimeters.

At low flow rates of CO or CO- $\text{CO}_2$  mixtures the rates of reduction were found to depend on the gas flow rate and increased with the increasing flow rate (16, 17, 18) till there was no more influence. At this stage, reagent starvation as well as mass transfer in the gas phase has significant influence on the reduction rate.

It was observed that the following equation is applicable for the reduction of iron oxides by CO (13):

$$1 - (1-f)^{1/3} = kt \quad \dots \dots \dots \quad (1-4)$$

where  $f$  = fractional reduction =  $\frac{\text{X}_{\text{Reduction}}}{100}$

$t$  = time

and  $k$  = constant.

For chemical control,  $K$  of equation (1-4) should be inversely proportional to the diameter of the specimen. This was observed in some cases (20) but Bickeloo and Clarke (18) found it to be independent of the size of the specimen. Khalafalla (19) found a marked promoter action of impurity oxides on the reduction of small  $\text{Fe}_2\text{O}_3$  particles (-4 mesh to plus 5 mesh) by CO. The extent of reaction rate enhancement was proportional to the ionic radius and

electronic charge of the promoter additive. This pointed out to chemical control.

The values of activation energy were variously found as 0.8 Kcal/mole (15), 13.9 Kcal/mole (16), 32.50 Kcal/mole (19) Khanifalla (19) found an unusually large activation energy (30-50 Kcal/mole) for reduction of coarse and crystalline FeO and  $Fe_3O_4$ . He attributed it to a large negative heat of adsorption of CO on the oxide surface.

It is recognized that the reduction process is complex. Such complexity arises from various sources. The product layer is porous and the diffusion process through the pores is influenced by the pore texture, which again depend on a number of factors. In addition, swelling of pellets, cracking during reduction, recrystallization of the reduced iron layer and the presence of unreduced iron oxide islands add to the complexity further.

### B-2-II) Kinetic aspects of gasification of carbon by CO<sub>2</sub>

Cokes, carbon and synthetic graphites are highly porous with pores ranging from about  $10 \text{ \AA}$  to several microns in diameter. The kinetic steps involved are gas film diffusion, diffusion through pores and chemical reaction at the gas-solid interface. It has been established that the chemical reaction is exclusively rate controlling below  $1100^\circ\text{C}$ , if the size of the graphite is not too large (diameter less than 1 cm.) such a conclusion has been arrived at from evidences such as high activation energy (60-90 Kcal/mole) and strong influence of solid and gaseous impurities even in trace quantities.

The rate of gasification decreases enormously with increase in percentage of CO in the gas. The rate with pure  $\text{CO}_2$  at 1 atmosphere has been found to be 100 times larger compared to a gas of 90 percent CO, 10 percent  $\text{CO}_2$  at  $900^\circ\text{C}$  (21).

In presence of catalyst the activation energy of the gasification reaction has been found to be as low as 15 Kcal/mole (22).

Walker and co-workers (23) found that the iron is an effective catalyst only when it is present as metallic iron mixed with a little FeO. The explanation put forward contends that the oxygen transfer at the graphite surface is enhanced by alternate oxidation of Fe and reduction of FeO. The catalytic activity is helped by mobility of oxygen on the metal surface. Ni and Co also exhibit similar catalytic action.

### 2.2. III Kinetic aspects of reduction of iron oxides by carbon

Amongst the investigations on reaction of iron oxide with carbon, only Otsuka and Kunii (24), determined the instantaneous rates of oxygen and carbon loss. They used 99 pet. pure  $\text{Fe}_2\text{O}_3$  which was prepared by roasting of iron nitrate at  $800^\circ\text{C}$ . The porous ferric oxide obtained had a specific gravity of 4.7 graphite employed for the reduction was electrode graphite (99.9%) with specific gravity of 2.2 and 31 pet. of pore volume. Standard tests sample of mixture contained 0.6 grams of  $\text{Fe}_2\text{O}_3$  and 0.2 grams of graphite. It was mixed and packed in silica bucket (void fraction 0.8) which was suspended by a platinum chain.

During the reaction, gaseous products were continuously removed by a nitrogen stream. At suitable intervals gas samples were analysed by gas-chromatograph. Overall reaction rate was calculated from the flow rate of the gas produced from the reacting solids.

They found that the reduction occurred in two stages. First stage was the formation of FeO from  $\text{Fe}_2\text{O}_3$  and the second stage was reduction of FeO to metallic Fe. They also observed an increase in the reduction rate after approximately 33 pct reduction which corresponds to complete conversion to FeO. Fig. (1-3) presents typical curves. The first stage had a high activation energy (35.75 Kcal/mole). From this it was concluded that the gasification reaction was rate controlling since the latter also has a high activation energy. There were further proofs for this. The rate increased when the particle size of the graphite was less and it was independent of the particle size of  $\text{Fe}_2\text{O}_3$ .

The increase of rate at the FeO stage could occur only if the carbon solution reaction was accelerated. So it was interpreted that the metallic Fe produced at the surface of the carbon had the catalytic effect on the gasification reaction. This was supported by the low activation energy for the second stage (15.23.5 Kcal/mole.).

The change in the gas composition as reduction proceeded is shown against composition in equilibrium with various oxide mixtures. In fig 1-4 It is evident that the gas was not reducing enough to allow formation of metallic Fe at early stage.

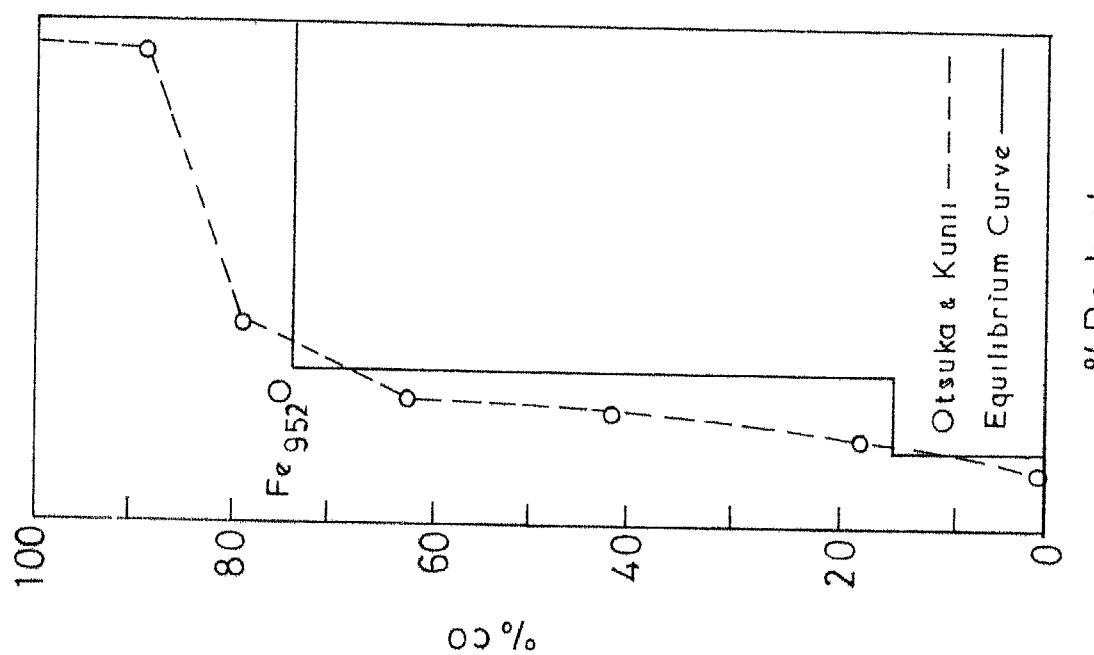


FIG 1.4

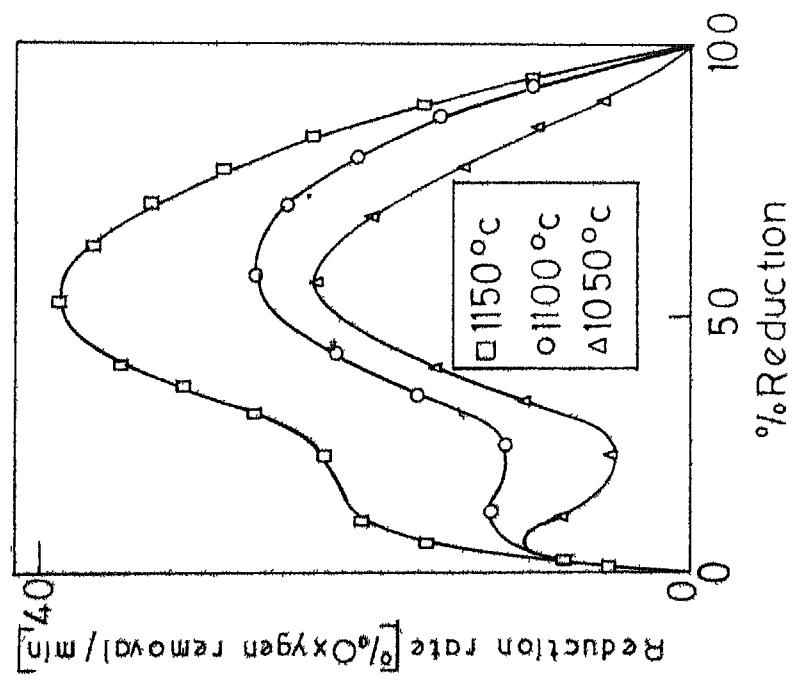


FIG 1.3

Thus the major conclusions drawn by Otsuka and Kunii were that:

- 1) Gasification reaction is the rate controlling and
- 2) reduced iron had catalytic effect on the rate of the reaction.

Besides Otsuka and Kunii, Rao (25) also investigated this reaction and came to the conclusion that gasification reaction is rate controlling.

Since the gasification reaction is chemically controlled, the rate of the reaction is altered by the impurities. This in turn affects the reduction of the iron oxides. Some impurities catalyze the reduction reaction itself.

T.P. Prasad and B.R. Sont (26) have reported that the alkali and alkaline earth salts accelerate the rate of reduction e.g. barium carbonate catalyses the gasification reaction and calcium oxide catalyses the reduction reaction. The accelerating effect of the alkali and the alkaline earth metals was perhaps due to the electronic interaction between the adsorbed oxides of these metals and the oxides being reduced.

While both sodium and potassium carbonates accelerate the reduction,  $\text{Na}_2\text{CO}_3$  is found to be more effective. This was attributed to the formation of surface active compounds and interaction of sodium ions or atoms.

The rate of reduction also depends on the nature of the carbon used for reduction. The reduction rate was higher with charcoal than with graphite. The activity of carbon also reflects in the degree of reduction.

Certain solutes were found to act as retarders. Oxides of Mg, Ti, Al and Si retarded the rate of reduction. The decelerating effect of the aluminium oxide and silica was attributed to the formation of aluminate and silicate.

The study by Otsuka and Kunii is the most comprehensive so far. However their conclusions cannot be held to be generally valid for all the types of materials without corroborating evidence. Also they took too little quantity of graphite. So chances are that the graphite got exhausted before the completion of reduction.

### C) Plan of the work:

The following things were decided upon.

- 1) To complete the fabrication of oxygen sensor which was initiated by A.K. Sengupta alongwith the gas train to purify the gases which will be fed to the oxygen sensor for testing purposes.
- 2) To test its performance using nitrogen oxygen mixtures at various temperatures and concentrations of the oxygen in the mixture.
- 3) To fabricate the reaction cell for the reduction of iron ore from Rajbara mines, Durg, by graphite.
- 4) To arrange for the measurements of instantaneous rates of reduction (rate of oxygen removal from ore) and rate of gasification (rate of carbon loss from graphite). It was planned to accomplish this in the following way.

Precision capillary flow-meters were planned to use in order to know the flow rate of CO-CO<sub>2</sub> gas mixture generated because

of the reaction of iron ore and graphite. The oxygen sensor then could measure the oxygen potential of the gas which in turn would give the CO/CO<sub>2</sub> ratio as discussed in section (B-1-1). Once the flow rate of gases and the CO/CO ratio is known the rates of evolution of CO and CO<sub>2</sub> individually and hence the instantaneous rates of the carbon and the oxygen removal can be calculated. To obtain the cumulative loss of carbon and oxygen, numerical integration was thought of.

**B. Correlation and interpretation of the data obtained.**

## CHAPTER II

## Apparatus

A) Oxygen Sensor:

$\text{ZrO}_2 + 10$  mole pct.  $\text{CaO}$  in the form of a tube was used as the solid electrolyte with following dimensions ( $0.95$  cm I.D.  $\times$   $1.27$  O.D.  $\times 45.8$  cms long). It had closed, flat end. It was supplied by Zirconium Corporation of America. It was checked for leaks under vacuum and was confirmed to be vacuum tight. The closed end was platinumized inside as well as outside by applying two successive coatings of the platinum paste and heating it to around  $900^\circ\text{C}$ .

The fig 2-1 shows the details of the oxygen sensor and in fig 2-2 combined assembly of the oxygen sensor and the gas-train is shown.

15

Quartz tube of/ $\text{mm}$  I.D. was used as an enclosure to the S.E. tube with a constriction at the middle, against which the S.E. tube rested. The other part of the quartz tube was used as preheating chamber. A pt/pt-10% Rh thermocouple was inserted through the preheating chamber, the tip of which was in contact with the S.E. tube. The pt/10% Rh wire of the thermocouple itself was used as one of the lead wires. To improve the contact a small piece of a pt-wire joined to the thermocouple bead was coiled and kept in between the quartz constriction and the S.E. tube which pressed against the former.

A two hole alumina rod (.635 cm. O.D.) was used inside the S.E. tube to hold the pt-10% Rh lead wire and to transport the reference gas into the cell. The tip of this wire was also coiled to

improve the contact. Tygon tubing was used for all the joints.

To further improve the contact between the lead wires and the -S.E. tube, springs were used, which were supported by the hooks on the quartz tube one end and the brass head fitted on the alumina rod at the other.

To eliminate electrical interference from the furnace windings and to avoid the pick up of other stray emfs a grounded inconel tube surrounding the quartz tube, was inserted into the furnace.

The design is similar to that of Bessell and Flenges (27) with some modifications. Speciality of this design is that the linear velocity of gas at the constriction can be made high.

The furnace employed for the heating of the S.E. cell was a horizontal tube furnace, which could attain a maximum temperature of about  $1100^{\circ}\text{C}$ . Magnesia asbestos powder along with hot face insulating bricks were used for insulation purposes.

Specifications of the furnace were:

Maximum power rating = 1.0 kw.

Length of the furnace = 45.7 cm

Outside diameter = 29.2 cm.

Heating element - Kanthal resistance wire

(BSW 16) having a resistivity of 0.01115  $\mu\text{ohm}$  cm

The furnace was fixed on a slotted angle frame work with castor wheels to make it portable. It could be moved vertically to adjust position. Electrical points were fitted on the trolley itself.

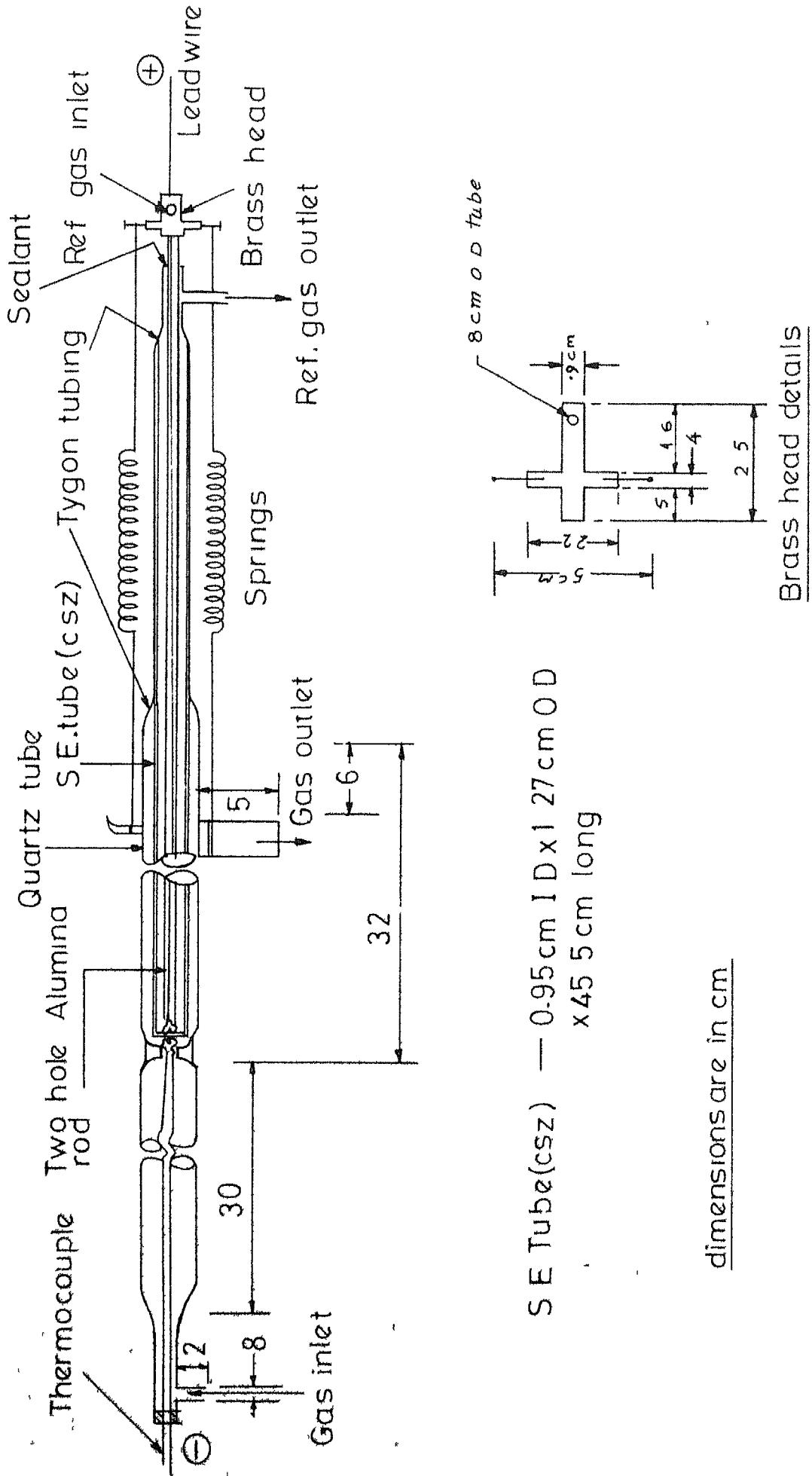


FIG 21

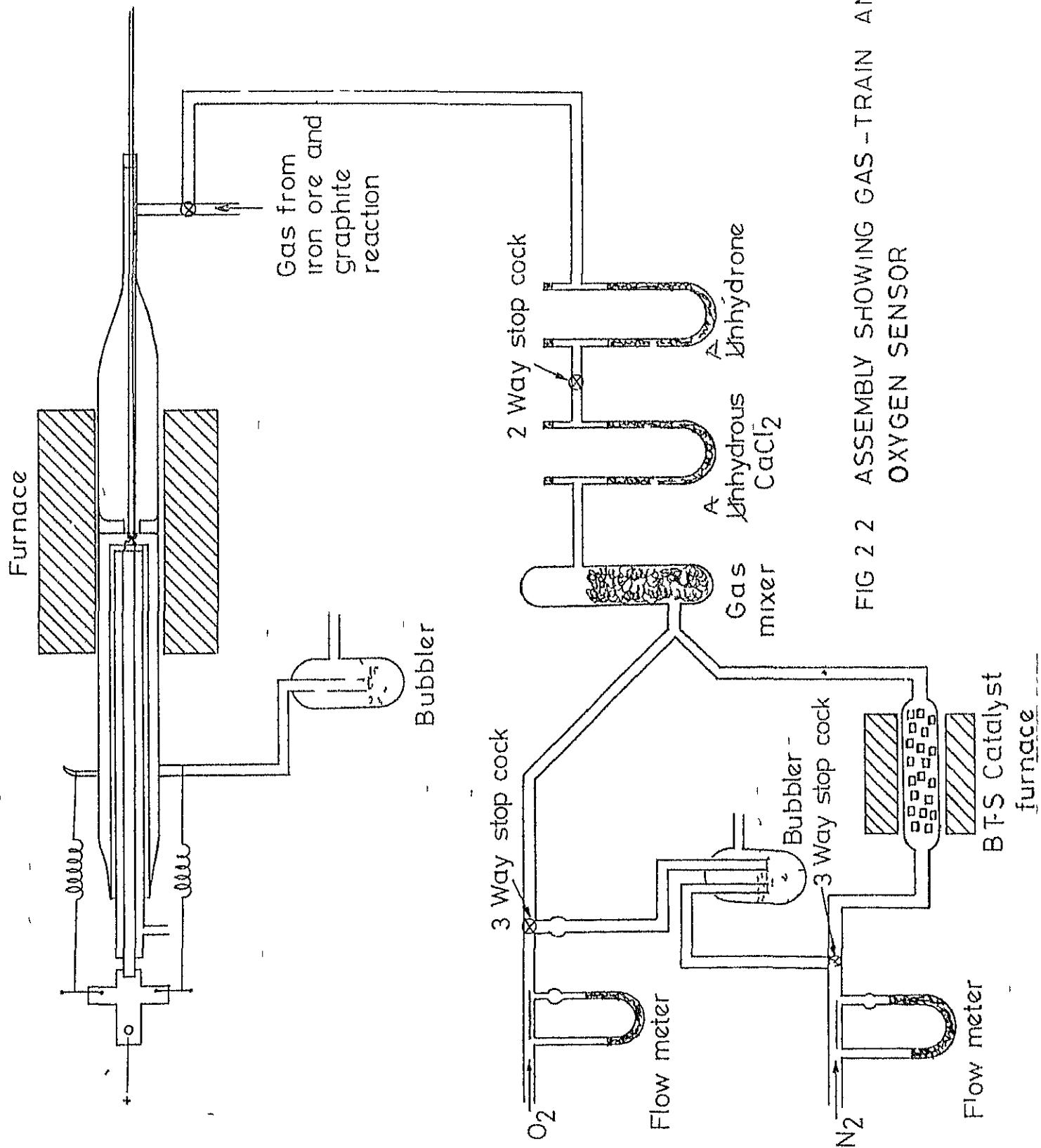
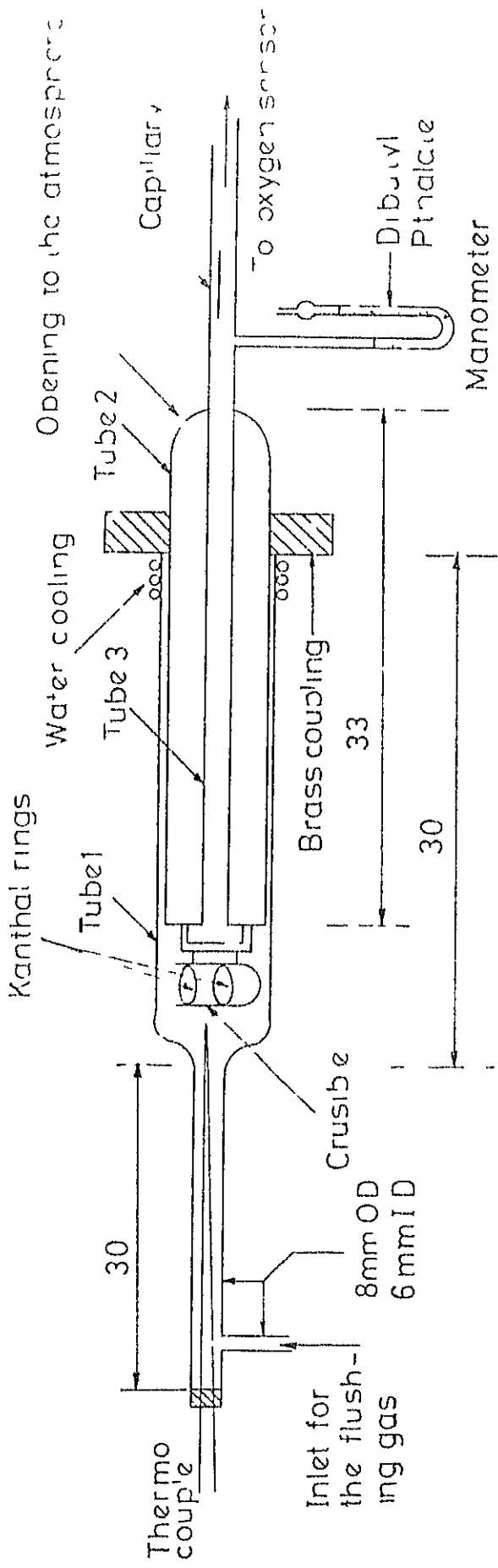


FIG 2 2 ASSEMBLY SHOWING GAS - TRAIN AND OXYGEN SENSOR



Tube 1 18mm ID 22mm OD  
 Tube 2 17.3mm OD  
 Tube 3 5mm ID  
 Crucible 13mm OD 13mm height

FIG 2.3 APPARATUS FOR IRON ORE - GRAPHITE REACTION

The lower portion of the trolley was used to keep vacum-  
ace, microvoltmeter for emf measurement and also for the gas train  
which was employed to purify the gas before passing it through the  
solid electrolyte assembly.

Cold junction arrangement for the thermocouple was as follows. The two ends of the compensating lead wires coming from the thermocouple were dipped into the small mercury pools which were kept immersed in water in a Dewar flask. A thermometer was used to measure the temp of the water.

For measurement of the emf developed, philips microvoltmeter with the following specifications was employed. D.C.  
Microvoltmeter pp 9004.

Ranges: 1M  $\Omega$  Input Impedance = 0.1 mV - 10V

100M  $\Omega$  Input Impedance= 10mV-1000V

Temperature was adjusted manually by a valve.

### 3) Ore-Carbon reaction assembly:

3-1) Since the amount of gas generated from the reaction of the iron ore and graphite was expected to be small, the minimum possible dead volume was aimed at in designing the reaction assembly Fig. (2-3) shows this.

An 18 mm I.D. and 22 mm. O.D. translucent quartz tube of 30 cm. length (tube 1) was employed as the reaction tube. To this a 6 mm I.D. translucent quartz tube was connected at one end. Through the latter tube a pt/pt-10%th thermocouple was inserted, insulated by a 0.15 cm single bore alumina sheath. The 6 mm silica

tube was also employed as an inlet for the purging gas which was passed over the sample during the pre-heating period. Cold junction arrangements were made for the thermocouple as in the previous case.

A 17.3 mm O.D. silica tube (tube 2) had both the ends closed except for a 5 mm I.D. (tube 3) silica tube concentrically joined to it. It had a quartz hook at one end to which a ring made out of kenthal heating element wire was tied. A quartz crucible with the sample (ore and carbon) was fitted in this ring. Thus the 17.3 mm tube helped in inserting the crucible as well as for taking it out. The inner 5 mm dia tube served as the outlet for the gases.

To seal the gap between tube no. 1 and 2, a water cooled brass coupling was employed. The coupling also facilitated the axial movement of tube 2 in tube 1 without letting any air in. A globar furnace was used for heating purpose.

The out let of tube 3 was connected to a capillary with a simple liquid (di butyl phthalate) manometer in between with the help of a 3 mm. I.D. tube. After the capillary again, a 3 mm I.D. tube led was used to lead the gas to the oxygen sensor. Arrangements were made to mix this gas with an inert gas just before it entered the oxygen sensor. Thus the gas mixture generated in the reaction cell flushed out fast through the oxygen sensor so as to allow measurement of instantaneous gas composition. This ensured correct CO/CO<sub>2</sub> ratio measurement at a particular time to a considerable extent.

The capillary along with the manometer served as a capillary flowmeter. A set of capillaries was used to cover the desired ranges of flow.

The oxygen sensor and the reaction assembly were kept as close as possible in order to minimize the length of the connecting tube so as to cut down the volume.

## CHAPTER III

EXPERIMENTAL PROCEDURES AND MATERIALSA) Procedure for testing of the oxygen sensor:

Inert gas oxygen mixture ( $N_2+O_2$ ) was employed for testing. The gas train employed for purification of these gases consisted of the flow meters, B.T.S. catalyst (obtained from BASF, Germany) furnace for oxygen removal, gas mixers to mix the gases before feeding it to the cell and U-tubes containing anhydrous  $CaCl_2$  and anhydrene to remove the moisture. A bubbler was also used to bypass the gas. The gas mixers consisted of a glass column filled with glass-beads.

Temperature of the solid electrolyte cell, percentage oxygen in the mixture and the flowrate of the gas were the variables. The flowmeters on the  $N_2$  and  $O_2$  lines were calibrated for the respective gases.

The flowmeter reading for both the gases were noted from which the oxygen contents in the mixtures were calculated. The system was allowed to attain steady state after which the steady emf, shown by the microvoltmeter was noted. Temperature was also measured. The microvoltmeter was calibrated with the help of the potentiometer for the necessary correction to the measured emf. When the corrected emf. and the cell temperature were known, corresponding  $PCO_2$  could be calculated by using equation (1-1).

The pct. oxygen obtained from flow-meter readings and from the measurement with oxygen sensor were compared in order

to examine the preaction of the sensor.

Sometimes air was used as the sample gas. In all the measurements pure  $O_2$  was the reference gas.

Sometimes the sensor chamber was evacuated when switching from one composition to the other, especially at low flow rates of  $N_2$  and  $O_2$ .

Attempts were also made to analyse the gas by gas chromatograph. In these cases the three values of pet. oxygen obtained from 1) gas chromatograph 2) flow-meters and 3) oxygen sensor were compared.

### b) Reduction of iron-ore with graphite:

Iron ore of Rajhara mines (Burg) was chosen for these experiments. It had the following analysis: Fe- 66.1%,  $SiO_2$ - 1.64%,  $Al_2O_3$ - 3.8%,  $TiO_2$ - absent.  $Fe^{+2}$  ions could not be traced. From this the oxygen content of the ore was estimated to be 28.3 wt. per cent which matched with the oxygen content calculated from weight loss by hydrogen reduction. The ore was found to contain 3.6 wt. moisture. This moisture was chemically held and could be removed only by heating to a higher temperature for at least 3 minutes. The imported low ash electrode graphite supplied by Nevinchandra and company was used for the experiments. Total ash content was estimated to be 1.12 per cent. The size of the graphite chosen was -200 mesh. Experiments were conducted at temperatures of approximately  $935^\circ C$ ,  $975^\circ C$ ,  $1015^\circ C$  and  $1050^\circ C$ . Two sizes of the iron ore were chosen: i) -325 mesh powder ii) 8 mm diameter pellets.

### B-2 Preparation of pellets

The ore was mixed with appropriate amount of water. Green pellets were made by hand-rolling. They were dried in an oven at about  $100^{\circ}\text{C}$  for sometime and then fired to  $900^{\circ}\text{C}$  for about 2 hours. The dried iron ore powder, graphite and pellets were stored in a desiccator.

### B-3 Preparation of the sample

For the experiments approximately one gm. iron ore was mixed with 0.4 gm graphite powder and then filled in the quartz crucible with intermittent hand-rolling. The crucible was weighed with and without the sample to know the initial weight of the sample. Then the crucible was fitted in the kenthal ring of tube 2 and inserted halfway in the heated reaction tube for preheating. During preheating an inert gas was made to flow over the sample to remove the moisture etc. Preheating was done for around five minutes. Then the flow of the inert gas was diverted to the oxygen sensor and the sample was pushed to the reaction zone. This time was noted down as the time for the reaction. After this at suitable intervals flow-meter readings and S.E. cell emf. were noted down. Emfs were measured by Phillips V.T.V. M. (Phillips CH 43708, s/n 1098 range-1mV-1000V) The reaction temperature and cell temperature were measured intermittently, V.T.V. M. was calibrated from time to time by potentiometer. The flow of the inert gas purging the oxygen sensor was kept at around 120-130 cc/min. When the reduction was nearly complete the reaction was stopped by taking out the sample. It was then weighed in order to know the weight loss.

In some cases the  $\text{N}_2$  flow caused some static pressure in the gas line from the reaction chamber by which some positive

pressure was shown in the manometer for zero flow. So from the observed  $\Delta h$  of the manometer, this zero reading was subtracted in order to obtain the actual  $\Delta h$ .

Some experiments were also done with pure  $\text{Fe}_2\text{O}_3$  and graphite.

The thermocouple used to measure the temperature of the reaction was calibrated with the help of a standard reference thermocouple, in the beginning, as well as at the end of the experiments. Initially it was matching with the reference one but was found to deviate from the calibrated curve at the end. So corresponding corrections were made to the measured reaction temperatures.

#### B-2 Calibration of capillary flowmeters

Four different capillaries, used for the flow measurement, were calibrated with argon at  $30^\circ\text{C}$ . The data were fed to the computer for fitting by the linear least square method and the equation thus obtained of the fitted curves were of the forms

$$Q = \text{slope} \times \Delta h + \text{constant}$$

Where  $Q$  = flow rate in cc/min.

and  $\Delta h$  = difference in height of liquid in the two limbs of the flowmeter in cms.

Since flow rate should be zero at zero  $\Delta h$ , the value of constant in the above equation must be zero. So corrections were made graphically. Table 3-1 shows the original and corrected equations for the different capillaries.

TABLE 3-1  
Calibration of capillaries by axon at 20°C

Capillary No.	$Q \propto V_0 \Delta h$ Correlation	$Q \propto V_0 \Delta h$ correlation after zero correction
1	$Q = 9.8339 \Delta h + 0.0669$	$Q = 9.83 \Delta h$
2	$Q = 3.7522 \Delta h + 0.1959$	$Q = 3.80 \Delta h$
3	$Q = 0.5807 \Delta h - 0.3974$	$Q = 0.5803 \Delta h$
4	$Q = 0.1842 \Delta h - 0.1106$	$Q = 0.18 \Delta h$

It may be noted that the differences in numerical values of the corrected and the original equations are small.

Since the gas coming out of the reaction chamber was CO-CO<sub>2</sub> mixture and not argon, corresponding viscosity corrections were made later on to get correct flowrates during the investigation.

## CHAPTER IV

### RESULTS AND DISCUSSIONS ON PERFORMANCE OF OXYGEN SENSORS

As mentioned in chapter 3, the first part of this investigation consisted of testing the performance of the oxygen sensor. This was done by mixtures of  $O_2$  and  $N_2$ . The oxygen content of this gas mixture was calculated from flow-meter readings and then compared with the oxygen sensor data. This was done at several oxygen contents and temperatures. Table 4-1, and fig. 4-1 present the data. In table 4-1, while calculating the percentage error in the measurement of oxygen concentration by the oxygen sensor, the values of oxygen concentration obtained from the flowmeter readings were assumed to be the correct ones.

These are the 50 pct readings in which the pct. error was below 20 pct. The remaining readings were rejected since the pct errors were more than 20 pct in those cases. Figs 4-1 and 4-2 show the pct error at various gas compositions and temperatures.

The possible sources of errors are:

#### **1) Improper electrode contact:**

If the lead wires have the improper contact with the platinized surface of the solid electrolyte tube, the emf measured will be less than the actual one and so the to calculated value of pct  $O_2$  will turn out to be higher. In some cases, application of the pressure by hand showed increase in the emf reading as more number of springs were employed to improve the contact.

#### **2) Electronic conduction in the solid electrolyte tube:**

If this is present, then also the emf measured will be

Table 4-1  
Performance of oxygen sensor

Gr. No.	Pipes rates ccs/min	Cell Temp °K	Cell MV	pet. O <sub>2</sub> from emf	pet. O <sub>2</sub> from flow meters <sup>a</sup>	pet. error
1.	Air	1026	35.4	21.47	20.9982	+ 2.30
2.	air	1033	35.5	21.95	20.9892	+ 4.49
3.	air	1113	35.75	22.53	20.9952	+ 7.35
4.	air	1121	36.5	22.06	20.9992	+ 5.11
5.	air	1177	33.2	22.17	20.9952	+ 5.63
6.	air	1180	37.1	23.24	20.9982	+ 10.75
7.	air	1191	39.7	21.28	20.9862	+ 1.39
8.	24.95	630	1022	72.4	5.538	+ 7.65
9.	7.95	1133	1030	108.3	0.6952	+ 9.59
10.	6.5	128	1039	68.0	6.981	- 3.77
11.	6.5	234	1041	79.1	2.703	+ 8.45
12.	9.0	142	1041	62.1	6.272	5.96
13.	6.57	81	1041	50.3	9.569	+ 10.68
14.	3.673	314.0	1043	98.0	1.153	+ 20.47
15.	30.07	630.0	1090	71.8	4.701	+ 11.0

16.	6.1428	69.6	1103	55.71	6.298	6.458	- 2.48
17.	5.071	129.	1114	78.5	4.121	3.782	+ 0.96
18.	5.071	204.	1115	85.5	2.869	2.425	+10.31
19.	5.8428	104.	1152	72.4	5.384	5.147	+ 4.61
20.	5.8428	147.5	1153	79.75	4.083	3.635	+ 9.44
21.	0.657	700.	1177	167.	0.1579	0.1209	+ 14.08
22.	7.86	58.	1179	53.2	12.5	11.95	+ 3.10
23.	6.5	128	1181	70.2	4.938	4.498	+11.12
24.	5.071	311.	1182	126.2	0.9561	0.9778	- 2.22
25.	18.57	380.	1182	75.0	5.258	4.858	+12.86
26.	7.8428	111.0	1184	70.0	6.45	6.412	-0.10
27.	7.8428	274.5	1185	80.7	2.864	2.703	+5.72
28.	6.5	257.5	1186	91.5	2.784	2.4821	+13.07
29.	2.786	279.0	1186	115.4	1.065	0.9857	+9.54
30.	9.0	575	1248	114.5	1.601	1.542	+18.8

2 for air pot. O<sub>2</sub> was calculated assuming 50% humidity at 780 mm Hg and 25°C.

Calibration for air at various temperatures

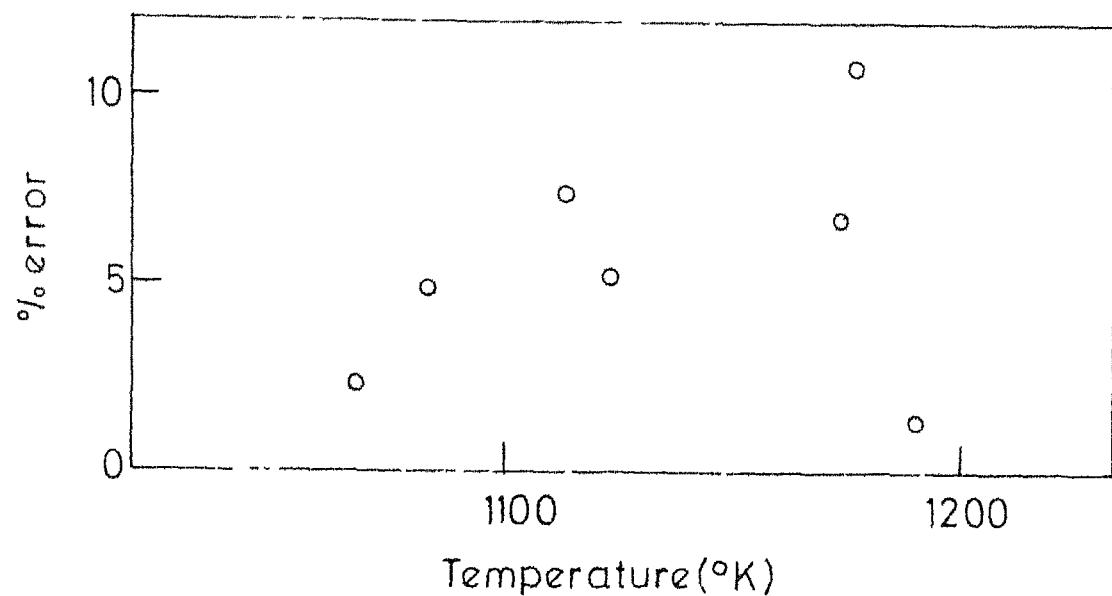
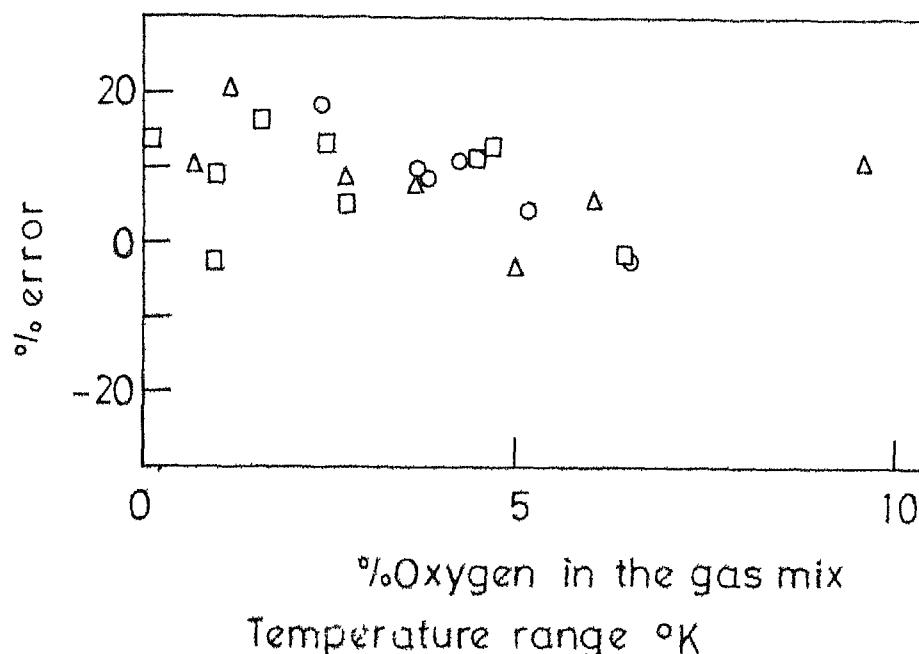


FIG 4-1



less than the actual. Since the flow rates were quite appreciable this source of error is not expected.

### 3) Scatter in the flowmeter readings:

If the actual amount of gas going into the system is different from that of the value calculated from the flowmeter calibration curve, error will be introduced in the calculation of oxygen concentration. Also the error in the measurement of  $\Delta h$  will introduce error in calculating oxygen concentration. Flowmeter calibrations were repeated in order to minimize this source of error.

### 4) Error in temperature measurement:

The thermocouple used was calibrated with the standard reference thermocouple and was found to be reading the correct temperature. So this error can be assumed to be absent.

### 5) Insufficient pre-heating of the flowing gas:

If the gas velocity is too high, it may not get heated to the cell temperature properly. So the system will not be in equilibrium which is assumed to be so in further calculations. Also it may cool down the outer portion of the solid electrolyte tube, causing the temperature gradient  $\frac{d\text{in}}{\text{tube}}$  itself. So the measurements made will be erroneous. However at low flow rates also errors were present.

### 6) Leak in the gas train or apparatus:

If there is any leak after the flow meter in the pure gas line, the actual gas getting mixed will be different from what is being measured which will cause the error in oxygen concentration. Also if the air is leaking in, it will also change the oxygen concentration. To get rid of this sort of error attempts were

made to make it leak proof. Still tiny leaks were present which could not be detected. However the leakage rate was hardly 2-3 ccs/min and it was outwardly. Therefore it is not expected to affect the readings.

7) Errors in potentiometers and microvoltmeter measurements of emf:

Errors in microvoltmeter readings were minimized by point to point calibration with potentiometer all the time.

To summarize, the improper electrode contact and the scatter of the flow meters especially at low oxygen may be the major sources of error.

Since the oxygen sensor was to be used to measure the CO/CO<sub>2</sub> ratio of the gases produced from the reaction of iron ore and graphite, doubt arose about the accuracy of the ratio measurement and of the further calculations of the rate of oxygen and carbon weight loss. For this, sample calculations were made to estimate the pct. error involved in oxygen loss rate ( $\dot{W}_O$ ) as a consequence of error in oxygen sensor measurement. Table 4-2 shows the results of these calculations.

Let the error in  $P_{O_2}$  measurement by oxygen sensor be 30 pct.

$$\text{Since } \frac{P_{CO_2}}{P_{CO}} \propto \sqrt{\frac{P_{CO_2}}{P_{O_2}}} \text{ error in } \frac{P_{CO_2}}{P_{CO}} \text{ is 15 pct.}$$

Thus it may be noted that from table 4-2 the errors in the rate of oxygen and carbon loss would be small. Gas composition also would not be in error seriously.

So it was decided to proceed with the study on reduction of iron ore by carbon.

Table 4-2  
Estimation of errors in oxygen loss rate

pct. CO <sub>2</sub> in CO-CO <sub>2</sub> mixture	Theoretical CO <sub>2</sub> /CO ratio	Measured CO <sub>2</sub> /CO after + 15 pct error	Measured gas comp. pct. CO <sub>2</sub>	Error in %, pct.
10	1/9 = 0.11	0.127	11.2	+ 1.0
50	1/1 = 1	1.15	53.0	+ 2.2
90	9/1 = 9	10.35	91.2	+ 0.7

$$(\%) \propto (\text{Rate of flow of CO} + 2 \times \text{rate of flow of CO}_2)$$

## CHAPTER V

### Results of Iron-Ore-Graphite Reactions

Raw data consisted of the reaction temperature, weight of the sample mixture of iron ore and graphite,  $\Delta h$  readings of the capillary flow meter at suitable time intervals and corresponding emf ( $E$ ) of the oxygen sensor. However the values of  $E$  and  $\Delta h$  are hardly useful as such. Hence these were fed to the computer for the following calculations.

#### A) Calculation of CO/CO<sub>2</sub> ratio:

As mentioned before, equilibrium may be assumed to prevail for the following reaction in the oxygen sensor.



$$\therefore 2 \Delta G^\circ_{\text{CO}_2} - 2 \Delta G^\circ_{\text{CO}} = , \Delta G^\circ \quad (5.2)$$

For the reaction (5.1) equilibrium constant  $K$  is equal to

$$\left[ \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right]^2 \times \frac{1}{P_{\text{O}_2}} \quad \dots \quad (5.3)$$

$$\delta^\circ = -RT \ln K \quad (5.4)$$

where  $T$  = Oxygen sensor temperature, °K.

$$\therefore \delta^\circ = -RT \ln \left[ \left( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2 \times \frac{1}{P_{\text{O}_2}} \right]$$

$$\approx 4,606 T (2 \log \frac{P_{\text{CO}_2}}{P_{\text{CO}}} - \log P_{\text{O}_2}) \quad \dots \quad (5.5)$$

Since the reference gas in the oxygen sensor had approximately 0.96 fraction of oxygen:

$$\log \frac{P_{O_2}}{P_{O_2}^0} = 20.199 - \frac{1}{T} \dots\dots \quad (5.6)$$

(from equation (1.1))

$$\therefore \Delta G^\circ = 4.6067 \left[ -0.02 - 20.199 \frac{1}{T} \right] - 9.2127 \log \frac{P_{CO_2}}{P_{CO}} \quad (5.7)$$

Table 3-1 shows the values of  $\Delta G^\circ$  at various temperatures. For the temperatures between  $1100^\circ - 1200^\circ K$  by interpolation:

$$\Delta G^\circ = -85,020 + 41.4 (T - 1200) \text{ Cal/mole...} \quad (5.8)$$

Thus once the oxygen sensor temperature and the cell emf (S) are known from equations (5-7) and (5-8), the CO/CO<sub>2</sub> ratio, which is the only unknown, can be determined.

### S) Correction for the capillary constant:

The calibration of the capillary was done with the help of argon. But since the gas flowing through the capillary during the reaction was a CO-CO<sub>2</sub> mixture instead of argon, the corresponding viscosity corrections had to be made. Viscosity of the mixture is a function of the individual mole fractions.

$$\mu_{mix} = \sum_{i=1}^2 \frac{x_i \cdot \mu_i}{\sum_{j=1}^2 x_j \phi_{ij}} \quad (5-9)$$

$$\text{where } \phi_{ij} = \frac{1}{\sqrt{8}} \left( 1 + \frac{\mu_i}{\mu_j} \right)^{1/2} \left[ 1 + \left( \frac{\mu_i}{\mu_j} \right)^{1/2} \left( \frac{M_i}{M_j} \right)^{1/4} \right]^2 \quad (5-10)$$

$M$  stands for the molecular weight and

$\mu$  stands for viscosities

on simplification for mixture of CO and CO<sub>2</sub> it gives

TABLE I

Values of  $\Delta G^\circ$  at various temperatures.

$T \text{ in } K$	$\Delta G^\circ_{CO}$ cal/mole	$\Delta G^\circ_{CO_2}$ cal/mole	$\Delta G^\circ$ cal/mole
1000	- 47,940	- 94,610	- 94,340
1100	- 50,080	- 94,640	- 99,100
1200	- 52,120	- 94,660	- 95,020
1300	- 54,240	- 94,680	- 89,860
1400	- 56,310	- 94,690	- 75,760

$$\mu_{\text{mix}} = \gamma_1 + \gamma_2 \quad \dots \dots \quad (5-11)$$

$$\text{where } \gamma_1 = \frac{1.002 \times 10^{-4} p_{\text{CO}}}{p_{\text{CO}} + 1.0831 p_{\text{CO}_2}} \quad \dots \dots \quad (5-12)$$

$$\text{and } \gamma_2 = \frac{1.493 \times 10^{-4} p_{\text{CO}_2}}{p_{\text{CO}_2} + 0.89974 p_{\text{CO}}} \quad \dots \dots \quad (5-13)$$

**C) Instantaneous rates of generation of CO and CO<sub>2</sub>**

Once the CO/CO<sub>2</sub> ratio is known and the corresponding viscosity correction made, total flow rate "Q" can be calculated by using the formulae

$$Q = (\text{Capillary constant}) \times \frac{\Delta h}{\mu_{\text{mix}}} \quad \dots \dots \quad (5-14)$$

$$\therefore Q_{\text{CO}} = Q \times \text{CO fraction cc/min.} \quad \dots \dots \dots \quad (5-15)$$

$$\text{and } Q_{\text{CO}_2} = Q \times \text{CO}_2 \text{ fraction cc/min.}$$

**D) Calculation of instantaneous rates of loss of carbon and oxygen:**

Since 1 mole of CO corresponds to 1 mole of carbon and oxygen each and one mole of CO<sub>2</sub> corresponds to 1 mole of carbon and 2 moles of oxygen.

$$\dot{W}_c = \text{Instantaneous rate of wt. loss of carbon}$$

$$= (Q_{\text{CO}} + Q_{\text{CO}_2}) \times 12 / (22400 \times 60) \quad \dots \dots \text{gms/sec} \quad (5-16)$$

$$\text{and } \dot{W}_O = \text{Instantaneous rate of wt. loss of oxygen}$$

$$= (Q_{\text{CO}} + 2 \times Q_{\text{CO}_2}) \times 16 / (22400 \times 60) \text{ gms/sec} \quad \dots \dots \quad (5-17)$$

### 5) Cumulative loss of 'C' and 'O' and net loss of 'O'

Since the oxygen content of the ore is determined to be 28.3 pct. by weight (30.0 pct. in case of pure  $\text{Fe}_2\text{O}_3$ ), by knowing the amount of ore or pure  $\text{Fe}_2\text{O}_3$  present in the sample, the total weight of the sample fed into the reaction chamber was known.

Trapezoidal rule was employed to numerically integrate instantaneous rates of removal of carbon or oxygen with respect to time. This gave the cumulative wt. loss of carbon and oxygen.

The percentage oxygen removal was obtained from the cumulative oxygen loss ( $\%_L$ ) and the total oxygen content at the beginning of the experiment.

The following things were printed in the output of the computer programme:

- 1) Time, min of oxygen burning rate (t), 0.1 to 100
- 2) Oxygen sensor out (E), volts
- 3) Instantaneous rate of 'O' wt. loss ( $\dot{\theta}_o$ ), gms/sec.
- 4) Cumulative oxygen weight loss ( $\theta_L$ ), gms
- 5) pct. oxygen loss
- 6) Instantaneous rates of 'C' wt. loss ( $\dot{\theta}_{\text{CO}}$ ) (in  $\dot{\theta}_o$ ) gms/sec.

The sum of the cumulative weight losses of oxygen and carbon at the end should match with the experimentally determined total weight loss ( $\theta_{\text{exp}}$ ) if the experimental errors are low.

Table 3-2 shows the experimental conditions of the various experiments performed with different materials.

Appendix- I presents the computer program.

Appendix- II gives a few sample computer printouts.

Table B-2  
Experimental conditions of various experiments

Expt. No.	Material	Reaction temp.	S.E. cell Temp. °C	$w_{T_B}$ gms	Total time of exper- iment, min	Capill- ary No.
1.	Ore powder +graphite	1047	847	0.5445	29	1
2.	—do—	1042	843	0.6113	29	1
3.	—do—	1019	836	0.3180	37	3
4.	—do—	974	821	0.3753	161	2
5.	—do—	939	826	0.1762	185	4
6.	Ore pellets +graphite	1084	831	0.3193	73	2
7.	—do—	1052	831	0.3489	49	2
8.	—do—	1019	831	0.4035	58	3
9.	—do—	972	818	0.4034	110	2
10.	pure $Fe_2O_3$ +graphite	955	823	0.4289	202	4
11.	—do—	939	828	0.3862	254	4

## CHAPTER VI

### DISCUSSIONS ON RESULTS OF IRON OXIDE-GRAPHITE REACTION

#### A) Reliability of the results:

As computer print out attached in Appendix II reveal, there are following problems with the results:

- i) CO content of gas is absurdly low ( $\approx 0.15$ )
- ii) Percent reductions are exceeding 100 in many cases. This is not possible.
- iii) In some experiments, notably those with pellets, gas evolution was appreciable even when the pet. reduction was close to 100 percent.

Computer calculations were also carried out assuming that the oxygen partial pressure as monitored by the sensor corresponded to the CO-CO<sub>2</sub>-O<sub>2</sub> equilibrium at the reaction temperature. Some of these calculations are presented in Appendix III. As may be noted, the CO-content of the gas varies between 0-10 pet, which is reasonable.

From this it was concluded that the equilibrium  $\text{CO(g)} + 1/2 \text{O}_2\text{(g)} = \text{CO}_2\text{(g)}$ .....(5-1) remained essentially 'frozen' even when the gas was being passed through the oxygen sensor. This would be due to comparatively lower temperature in the oxygen sensor and perhaps the slowness of the above reaction.

Therefore further consideration of the data were based upon the latter calculations; since it gave reasonable values of the gas composition. However, it was decided to ignore the gas composition data altogether. Rate of carbon gasification ( $\dot{n}_C$ ) is independent of the gas composition since one mole of CO as well as one mole of CO<sub>2</sub> contains one mole of carbon. So the  $\dot{n}_C$  can be obtained just by knowing the flow

rate of the gas and the gas composition is not required at all. Therefore, rate of gasification was used as a measure of the rate of reduction, for interpretation of data.

Tunkelogen and co-workers (28) have shown that rate of gasification is proportional to the weight of carbon. Therefore fractional rate of carbon gasification was preferred.

$$\text{Fractional } w'_c (\theta_{c,f}) = \frac{w}{\text{Original wt. of carbon in the mixture}} \quad \dots (6.1)$$

The data, as processed by assuming 'frozen'  $\text{CO}/-\text{CO}_2$  equilibrium were assessed on the basis of the following considerations,

- i) Is the qualitative nature of the variation of gas composition with pct reduction reasonable (as in fig. 1-4) ?
- ii) Is the final pct reduction less than 100 percent ?
- iii) Does the total weight loss as arrived by integration using Trapezoidal rule match with the experimental weight loss measurement ( $w_{TG}$ ) ?
- iv) Was the reaction continuing appreciably even when the pct reduction was more than 100 pct ?.

Table 6-1 summarizes some of these informations.

The experiments where experimental weight loss data were not available were rejected alongwith few others which were grossly irregular. The rest have been included in table 6-1. The experiments have been classified as good, satisfactory and poor.

(i) An experiment considered good had the following characteristics:

- i) The qualitative nature of variation of gas composition with pct reduction was reasonable.

TABLE 6.1

Calculations on the basis of frozen  $\text{CO}_2\text{-O}_2$  equilibrium

Expt. No.	Starting material	Reaction temp. °C.	Per cent loss	Total (Cr-O) loss calculated per cent loss	$\gamma_{\text{Fe}}$	Remark on data	Basis of correction
1.	ore powder + graphite	1047	152.7	0.7714	0.3445	S	100 per cent reduction
2.	-- + O <sub>2</sub> --	1042	165.6	0.6591	0.3113	S	-- -- --
3.	-- + O <sub>2</sub> --	1013	10.3	0.3180	0.4036	C	-- -- --
4.	-- + O <sub>2</sub> --	974	194.5	0.8323	0.5733	S	$\gamma = 3/1$
5.	-- + O <sub>2</sub> --	933	23.2	0.0394	0.1762	P	$\gamma = 1/1$
6.	Ore pellet + graphite	1034	131.9	0.6294	0.3193	C	100 per cent reduction
7.	-- + O <sub>2</sub> --	1052	81.1	0.3836	0.3485	C	$\gamma = 3/1$
8.	-- + O <sub>2</sub> --	1019	64.1	0.3657	0.4035	C	$\gamma = 2/1$
9.	-- + O <sub>2</sub> --	972	131.0	0.2264	0.4934	S	$\gamma = 2/1$
10.	pure Fe <sub>2</sub> O <sub>3</sub>	955	128.5	0.4196	0.4289	C	100 per cent reduction
11. 14% magnetite + graphite	938	126.1	0.3779	0.3362	C	-- -- --	

\* S - Satisfactory

C - Good

P - Poor.

- ii) Final pct. reduction was not too different from 100 pct.
- iii) Calculated and experimental weight loss matched reasonably.
- iv) The reaction more or less had subsided towards the end.

DO Corrections to processed data:

The above assessment pointed out that one of the likely sources of error was in the flow rate measurement at high flow-rates. In this case the gas perhaps did not cool to room temperature while passing through the flow meter causing the error in the flow measurement. Also erroneous gas composition would lead to erroneous viscosity values.

Based on all those assessments, it was felt that the final results should be corrected on the basis of the following assumptions.

- i) Experimental total weight loss ( $W_{Tg}$ ) is correct.
- ii) A reasonable CO-content of the gas can be guessed.
- iii) Pct reduction cannot exceed 100 pct.

Since causes and natures of errors etc. as used were not the same for all experiments, procedures for correction differed from experiment to experiment. However, they fall into the following two broad categories.

- i) For the experiments where the reaction had subsided, the last pct. reduction should correspond to 100 pct. appreciably. Hence the basis of correction was to assume that the last reading corresponds to 100 pct reduction.

$$W_C (\text{Corrected}) = W_{Tg} - 0.293 \times \text{wt. of ore} \dots \dots \quad (6-2)$$

$$\text{or} \quad (0.3) \times (\text{wt. of pure } Fe_2O_3)$$

$$i_C (\text{corrected}) = \frac{i_C (\text{corrected})}{i_C (\text{as per original calculation})} \times i_C (\text{uncorrected}) \quad (6-3)$$

$$\text{Corrected pet reduction} = \frac{\text{pet. reduction}}{\text{final pet reduction(original)}} \times 100$$

2) For experiments where gas evolution continued appreciably at the end, a certain average CO/CO<sub>2</sub> ratio (1/1, 3/2, 2/1 or 3/1), depending on reaction temperature was assumed as y. Then

$$\text{Since, CO fraction} = \frac{y}{1+y} \quad \dots \dots \quad (6.4 \text{ a})$$

$$\text{and CO}_2 \text{ fraction} = \frac{1}{1+y} \quad \dots \dots \quad (6.4 \text{ b})$$

$$\begin{aligned} \frac{\text{Moles of O lost}}{\text{Moles of C lost}} &= \frac{1/2 \cdot \frac{y}{1+y} + \frac{1}{1+y}}{\frac{y}{1+y} + \frac{1}{1+y}} \\ &= \frac{1/2 \cdot y + 1}{y + 1} \end{aligned} \quad (6.5)$$

$$\therefore w_0 = \frac{32}{12} \times \frac{y+2}{2(y+1)} \quad w_C \quad \dots \dots \quad (6.6)$$

$$\text{Also } w_{TE} = w_0 + w_C \quad \dots \dots \quad (6.7)$$

$$\text{Hence, } w_C \text{ (corrected)} = w_{TE} / \left( 1 + \frac{32}{12} \times \frac{y+2}{2(y+1)} \right) \quad (6.8)$$

$$w_0 \text{ (corrected)} = w_{TE} - w_C \text{ (corrected)} \quad \dots \dots \quad (6.9)$$

$w_C$  (corrected) is obtained from equation (6.3)

$$\text{pet. Reduction (corrected)} = \frac{w_0 \text{ (corrected)}}{w_0 \text{ (original)}} \times \text{pet reduction(original)} \quad (6.10)$$

If pet reduction (corrected)  $\approx 100$  the final reading was further normalized to 100 pet; otherwise not.

Appendix - IV presents corrected values of fractional carbon loss rate ( $\dot{w}_{C,f}$ ) and pet. reduction. Figures (6-1) to (6-4) show  $\dot{w}_{C,f}$  vs. pet. reduction curves for various experiments.

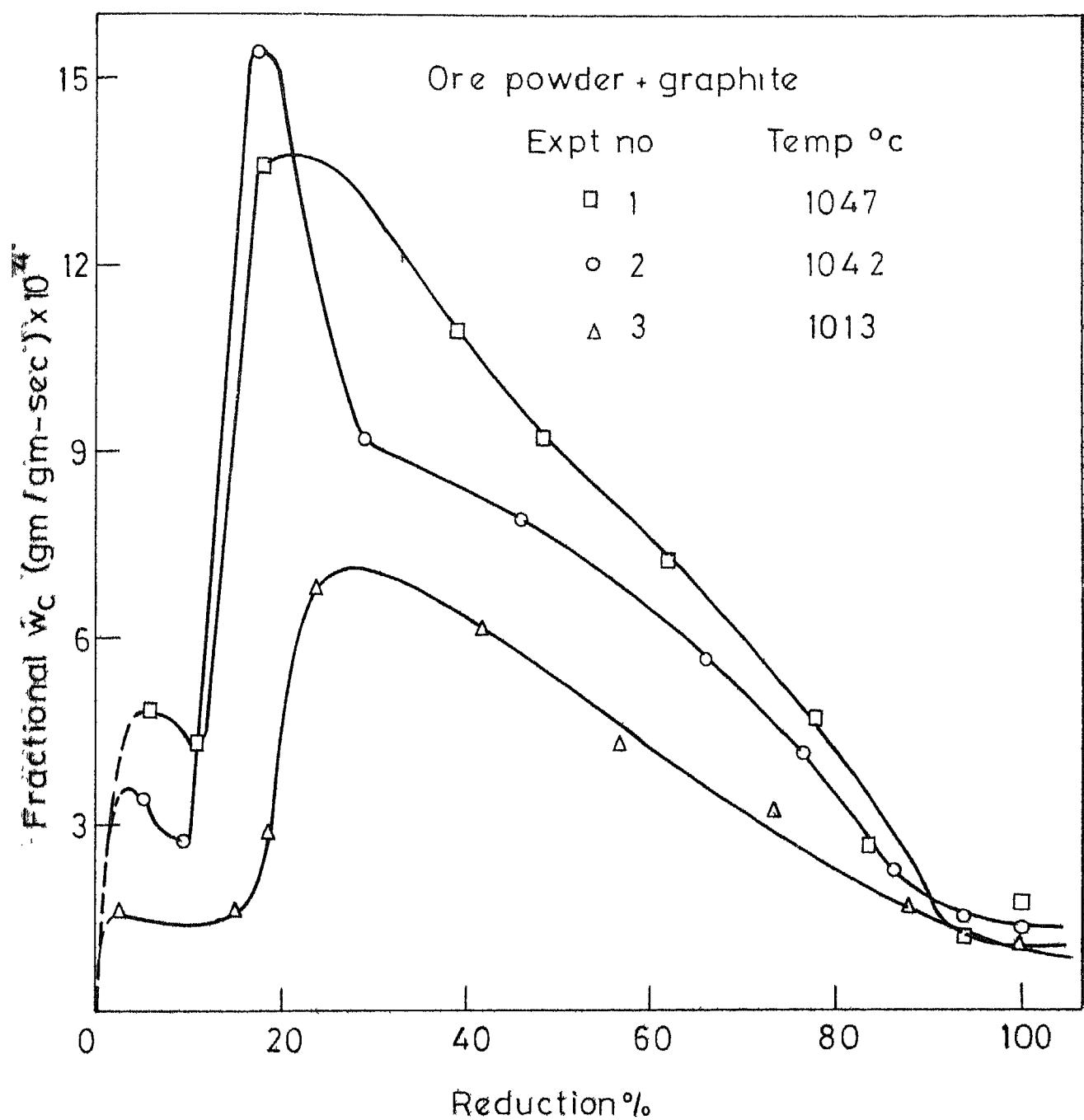


FIG 6-1

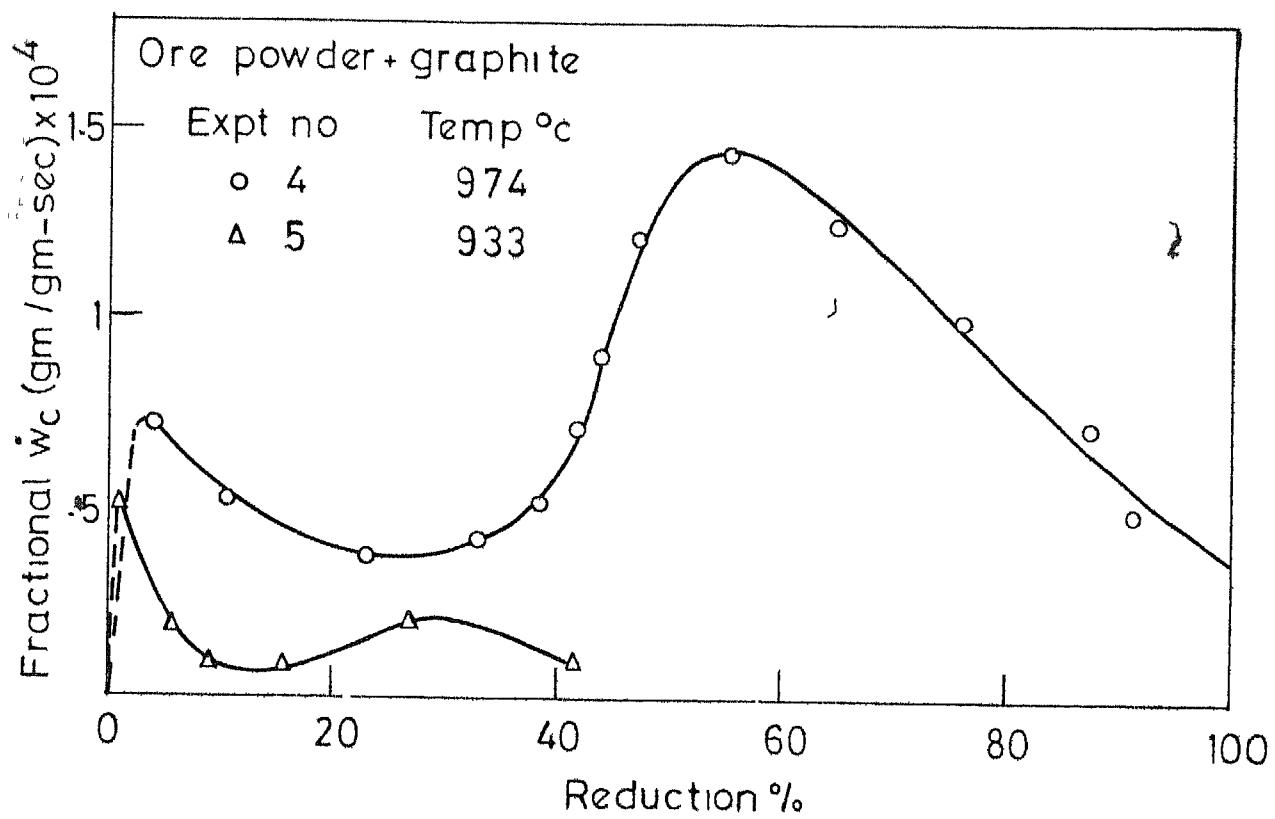


FIG. 6-2

IIT MUMBAI  
CENTRAL LIBRARY  
 Acc. No. A 45551

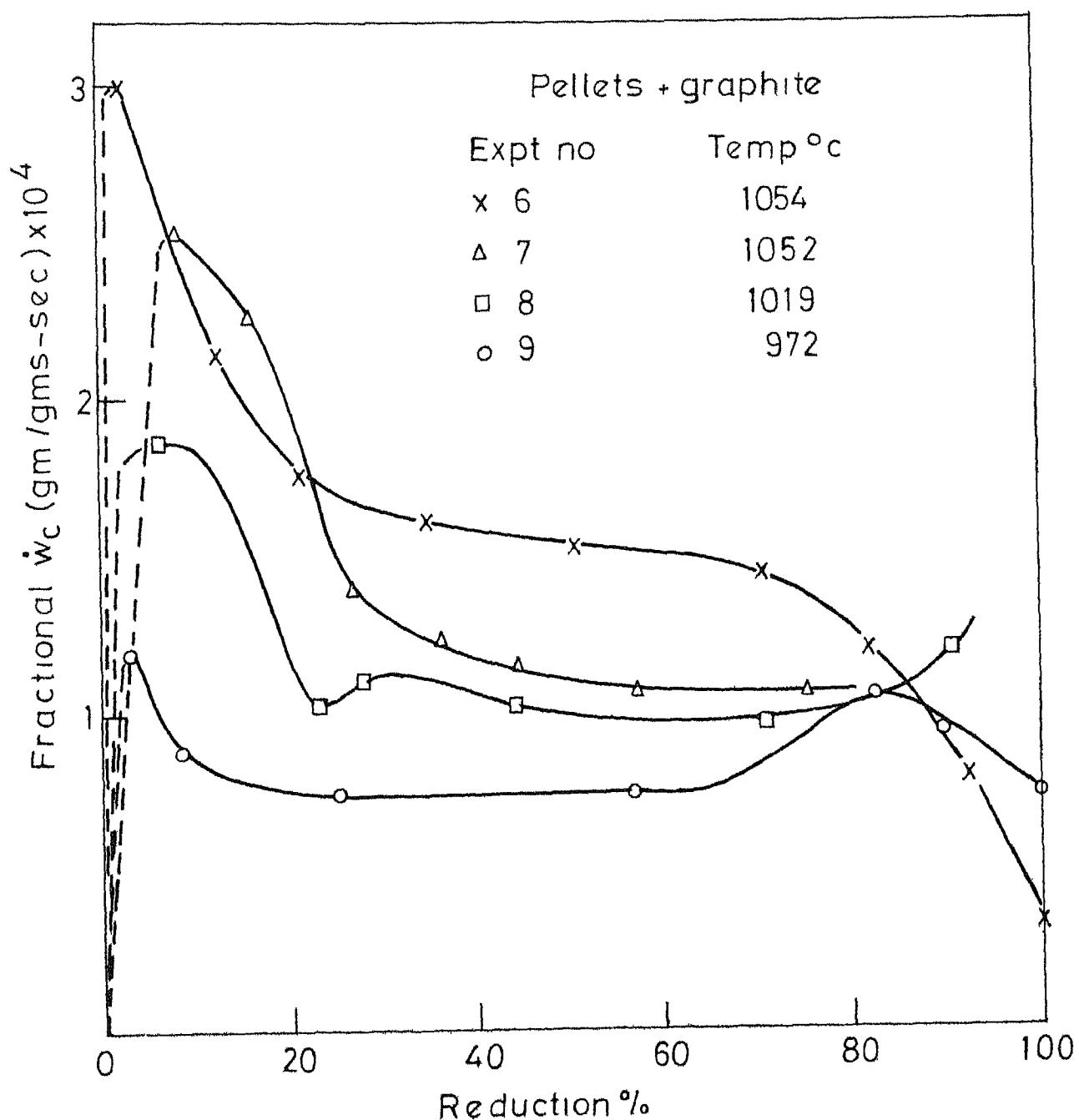


FIG. 6-3

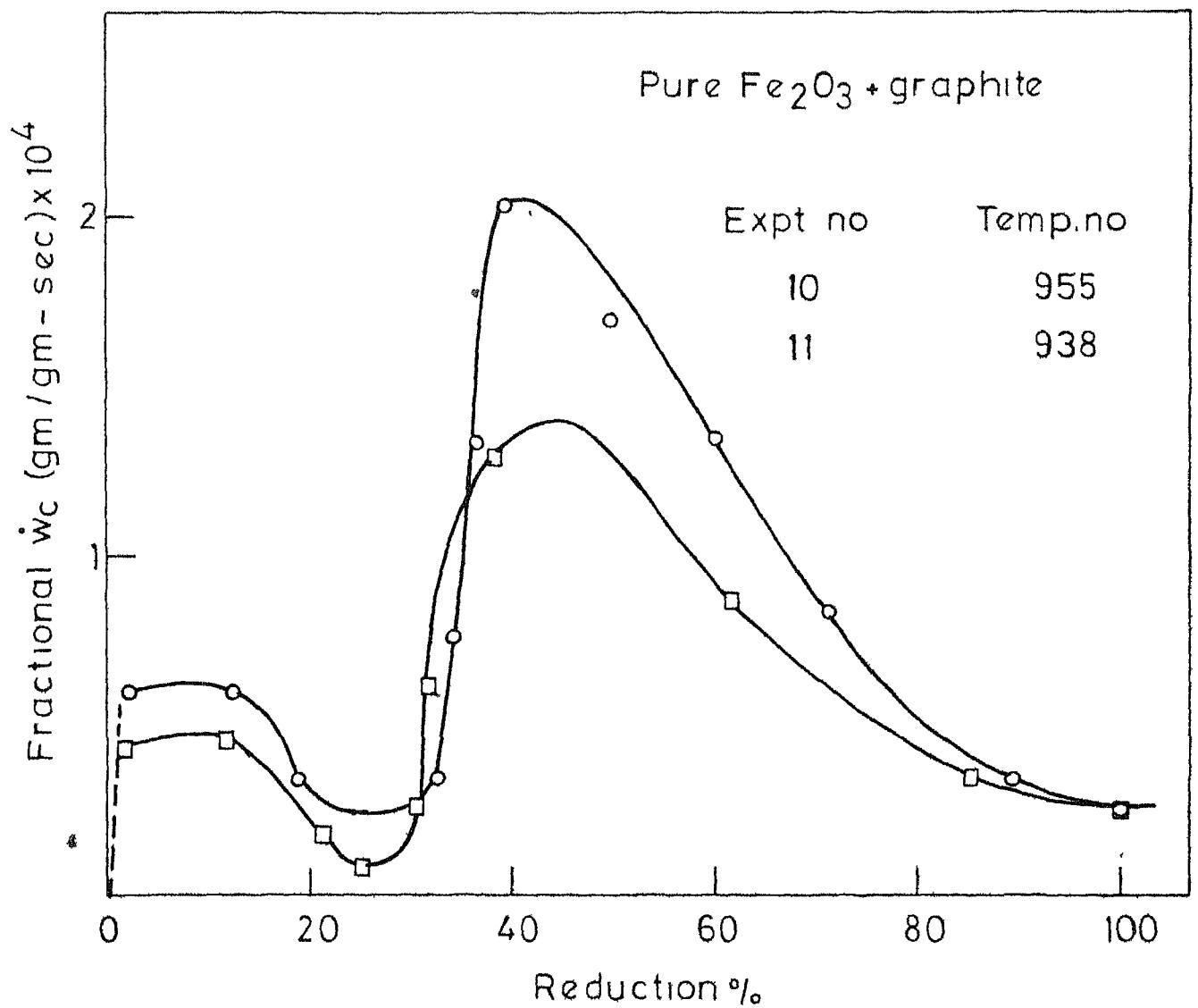
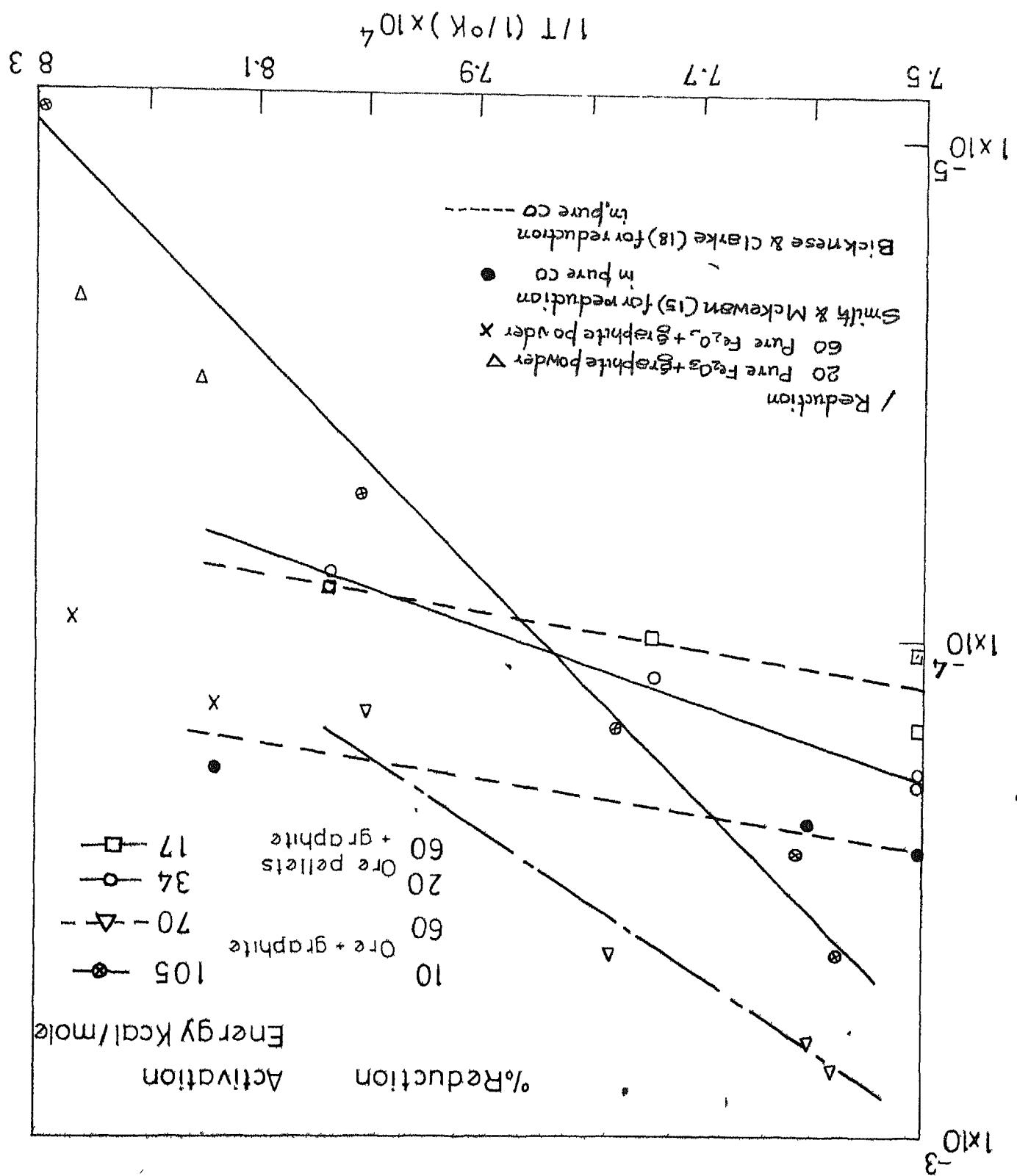


FIG. 6-4

FIG 6-5



**APPENDIX - I**

**COMPUTER PROGRAMME**



**A L P E D D A X - II**

**SAMPLE COMPUTER PRINTOUTS ASSUMING  
CO-CO<sub>2</sub>-O<sub>2</sub> EQUILIBRIUM AT OXYGEN SCR  
SCR TEMPERATURE.**

EXPERIMENT NO. = 4  
 REACTION TEMPERATURE = 574.0000  
 SOLID ELECTROLYTE CELL TEMPERATURE = 821.0000  
 CAPILLARY CONST = C.66C8E-03  
 WEIGHT OF THE C.R.E = C.9773

TIME (MINS)	VOLTS	DEL H (GM/S)	CC FRACTION	INS.O LOSS (GM/S/SEC)	CUM.C LOSS (GM/S)	PCT.D LCSS	INS.C LOSS (GM/S/SEC)
2.0	C.350	C.0000	C.0052E-01	0.0139	5.0227	0.3945E-04	C.3154E-04
4.0	C.150	C.8C	C.8419E-04	0.0196	7.073	0.3572E-04	C.3572E-04
5.0	C.155	C.8C	C.8419E-04	0.0245	8.9079	0.2763E-04	C.2763E-04
6.0	C.155	0.7C	0.0000	C.7367E-04	0.0294	0.6152	0.2763E-04
9.0	C.150	0.7C	0.0000	C.7367E-04	0.0426	5.4106	0.2763E-04
14.0	C.155	0.6C	0.0000	C.6314E-04	0.0631	22.8506	0.2368E-04
18.0	C.160	0.6C	0.0000	C.6314E-04	0.0783	28.5059	0.2506E-04
20.0	C.160	0.5C	0.0000	C.5262E-04	0.0852	30.822	0.1973E-04
25.0	C.155	C.5C	0.0000	C.5262E-04	0.0916	31.103	0.1973E-04
23.0	C.160	0.5C	0.0000	C.5262E-04	0.0947	4.2438	0.1973E-04
27.0	0.65	C.50	0.0000	C.5262E-04	C.3C73	38.849	0.1973E-04
29.0	C.170	C.5C	0.0000	C.5262E-04	0.1337	41.0950	0.1973E-04
36.0	C.170	C.6C	0.0000	C.5262E-04	0.1466	52.2335	0.1973E-04
31.0	C.175	C.6C	0.0000	C.6314E-04	0.3223	43.4922	0.2368E-04
34.0	C.180	0.6C	0.0000	C.6314E-04	0.3387	67.6047	0.2368E-04
35.0	C.170	0.6C	0.0000	C.6314E-04	0.3384	78.975	0.2368E-04
37.0	C.175	0.6C	0.0000	C.6314E-04	0.3430	81.7442	0.2368E-04
38.0	C.180	0.6C	0.0000	C.6314E-04	0.4468	93.080	0.2368E-04
40.0	C.185	0.6C	0.0000	C.6314E-04	0.4544	95.8207	0.2368E-04
41.0	C.220	0.7C	0.0000	C.7367E-04	0.4585	77.3047	0.2763E-04
42.0	C.180	0.8C	0.0000	C.6314E-04	0.4632	80.9923	0.3132E-04
43.0	C.850	1.0C	0.0849	C.9896E-04	0.4686	60.9845	0.3876E-04
44.0	C.860	1.0C	0.1029	C.1075E-03	0.4743	53.5936	0.4248E-04
45.0	C.870	1.2C	0.1342	C.1254E-03	0.4853	65.6208	0.4614E-04
46.0	C.880	1.4C	0.1652	C.1308E-03	0.4888	68.2330	0.5340E-04
47.0	0.895	1.5C	0.1943	C.1369E-03	0.4969	71.1842	0.5685E-04
48.0	C.900	1.6C	0.2114	C.1441E-03	0.2053	74.2322	0.6043E-04
49.0	C.900	1.7C	0.2184	C.1534E-03	0.2142	77.4364	0.6424E-04
50.0	C.900	2.0C	0.1801E-03	C.1801E-03	0.2142	81.074	0.7554E-04
51.0	C.895	2.1C	0.1916E-03	C.1916E-03	0.2354	85.3040	0.7955E-04
52.0	C.890	2.30	0.2124E-03	C.1782	0.2475	99.4870	0.8746E-04



0.47	0	0.780	0.5483E+04	0.7785
148	0	0.765	0.5205E+04	0.7816
149	0	0.755	0.5215E+04	0.7847
150	0	0.745	0.5225E+04	0.7879
151	0	0.745	0.5225E+04	0.7969
152	0	0.730	0.5235E+04	0.7910
153	0	0.735	0.5232E+04	0.7941
154	0	0.720	0.5240E+04	0.7973
155	0	0.715	0.5242E+04	0.7973
156	0	0.695	0.5249E+04	0.8067
157	0	0.660	0.5256E+04	0.8099
158	0	0.290	0.0000	0.5262E+04
159	0	0.280	0.0000	0.5262E+04
160	0	0.275	0.0000	0.5262E+04
161	0	0.250	0.0000	0.5262E+04
				TOTAL LOSS= 0.8223
				TOTAL C LOSS= 0.3255

EXPERIMENT NO. = 5  
 REACTION TEMPERATURE = 933.000C  
 SCLID ELECTROLYTE C-LI TEMPERATURE = 826.000C  
 CAPILLARY CONST = 26.08E-04  
 WEIGHT OF THE CRP = 0.9900

TIME (MINS)	VOLTS	DEL H (GMS)	CC FRACTION	INS-C LOSS (GMS/SEC)	CUM-C LOSS (GMS)	PCT.O LCSS	INS-C LOSS (GMS/SEC)
2.0	C.320	4.9C	C.0000	C.2059E-04	0.0014	0.4549	0.7645
4.0	C.125	4.0C	0.0009	C.2664E-04	0.0026	0.6277	0.6277
6.0	C.525	3.1C	0.0000	C.1288E-04	0.0045	1.5915	0.4893
7.0	C.125	2.5C	0.0000	C.1039E-04	0.0059	2.0907	0.3895
9.0	C.425	2.4C	0.0000	C.9970E-04	0.0074	2.5237	0.3739
12.0	C.425	2.2C	0.0000	C.8724E-04	0.0088	3.4212	0.3272
15.0	C.130	2.4C	0.0000	C.7893E-04	0.0104	3.6600	0.2960
17.0	C.120	2.6C	0.0000	C.6647E-04	0.0124	3.9744	0.2493
20.0	C.35	2.5C	0.0000	C.6231E-04	0.0144	4.2854	0.2437
22.0	C.40	3.0C	0.0000	C.5604E-04	0.0160	4.6352	0.2025
25.0	C.45	0.9C	0.0000	C.3739E-04	0.0185	4.9288	0.1402
27.0	C.40	2.0C	0.0000	C.4154E-04	0.0243	5.0978	0.1558
30.0	C.50	0.8C	0.0000	C.3235E-04	0.0250	5.3380	0.1246
34.0	C.55	C.9C	0.0000	C.2739E-04	0.0159	5.6455	0.1455
38.0	C.55	C.80	0.0000	C.3323E-04	0.0267	5.9430	0.1246
44.0	C.60	C.90	0.0000	C.3739E-04	0.0273	6.2659	0.1140
46.0	C.60	C.55	0.0000	C.4154E-04	0.0185	6.5975	0.1558
50.0	C.55	C.50	0.0000	C.4154E-04	0.0195	6.9435	0.1455
52.0	C.60	C.60	0.0000	C.4985E-04	0.0200	7.2444	0.1869
56.0	C.60	C.20	0.0000	C.4985E-04	0.0224	7.6914	0.1669
67.0	C.40	C.20	0.0000	C.4985E-04	0.0245	8.7455	0.1869
70.0	C.140	C.30	0.0000	C.5404E-04	0.0254	9.0794	0.2025
76.0	C.145	C.20	0.0000	C.5404E-04	0.0274	9.7120	0.2225
86.0	C.50	C.40	0.0000	C.5816E-04	0.0307	10.9741	0.2337
96.0	C.40	C.40	0.0000	C.5816E-04	0.0339	12.7404	0.2437
100.0	C.45	C.50	0.0000	C.6254E-04	0.0357	14.0766	0.2537
115.0	C.45	C.50	0.0000	C.6231E-04	0.0294	14.7855	0.2648
125.0	C.55	C.50	0.0000	C.7062E-04	0.0414	16.6031	0.2648
127.0	C.55	C.70	0.0000	C.7062E-04	0.0465	17.7402	0.2537
135.0	C.55	C.50	0.0000	C.6231E-04	0.0497	18.7402	0.2537
145.0	C.55	C.40	0.0000	C.5816E-04	0.0533	19.0351	0.2537

151.0	C.145	2.30	0.0000	C.5401E-03	0.0553
155.0	C.150	2.20	0.0000	0.4985E-03	0.0566
165.0	C.145	2.20	0.0000	0.4952E-03	0.0595
171.0	0.150	2.40	0.0000	0.4570E-03	0.0632
180.0	C.150	2.10	0.0000	0.4570E-03	0.0638
185.0	0.155	0.90	0.0000	0.2739E-03	0.0650

TOTAL O LOSS = C.0650  
TOTAL C LOSS = C.C244

EXPERIMENT NO. = 9  
 REACTION TEMPERATURE = 972.0000C  
 SOLID ELECTROLYTE CELL TEMPERATURE = 818.5000C  
 CAPILLARY CONST = C.66CBE.C3  
 WEIGHT OF THE CRE = 1.0025

TIME (MINS)	VOLTS	DEL H (GMS)	FRACTION (GMS)	CC FRACTION (GMS/SEC)	INS.G LCSS (GMS)	CUN.G LCSS (GMS)	PCT.G LCSS	INS.C LOSS (GMS/SEC)
3.0	0.450	0.80	0.0000	0.8439E-01	0.0301	0.5612	0.3157E-04	0.2765E-04
4.0	0.450	0.70	0.0000	0.7367E-01	0.0448	0.2353	0.2763E-04	0.2763E-04
5.0	0.445	0.70	0.0000	0.7367E-01	0.0453	0.7853	0.2763E-04	0.2568E-04
6.0	0.445	0.60	0.0000	0.6314E-01	0.0234	0.2150	0.2368E-04	0.2368E-04
7.0	0.450	0.60	0.0000	0.6554E-01	0.0272	0.5704	0.2368E-04	0.2368E-04
8.0	0.445	0.60	0.0000	0.6314E-01	0.0309	0.9058	0.2368E-04	0.2368E-04
9.0	0.430	0.60	0.0000	0.6314E-01	0.0347	2.2472	0.2368E-04	0.2368E-04
10.0	0.420	0.60	0.0000	0.6314E-01	0.0385	3.5746	0.2368E-04	0.2368E-04
11.0	0.410	0.60	0.0000	0.6314E-01	0.0423	4.9120	0.2368E-04	0.2368E-04
12.0	0.410	0.50	0.0000	0.5262E-01	0.0327	5.843	0.1973E-04	0.1973E-04
13.0	0.415	0.50	0.0000	0.5262E-01	0.0377	6.2613	0.1973E-04	0.1973E-04
14.0	0.420	0.50	0.0000	0.5262E-01	0.0423	6.9172E-01	0.1973E-04	0.1973E-04
15.0	0.420	0.50	0.0000	0.5262E-01	0.0469	7.5071	0.1973E-04	0.1973E-04
16.0	0.410	0.50	0.0000	0.5262E-01	0.0506	8.1422	0.1973E-04	0.1973E-04
17.0	0.405	0.50	0.0000	0.5262E-01	0.0542	8.8054	0.1973E-04	0.1973E-04
18.0	0.405	0.50	0.0000	0.5262E-01	0.0578	9.4914	0.1973E-04	0.1973E-04
19.0	0.405	0.50	0.0000	0.5262E-01	0.0614	10.1768	0.1973E-04	0.1973E-04
20.0	0.405	0.50	0.0000	0.5262E-01	0.0650	10.8726	0.1973E-04	0.1973E-04
21.0	0.405	0.50	0.0000	0.5262E-01	0.0686	11.5751	0.1973E-04	0.1973E-04
22.0	0.405	0.50	0.0000	0.5262E-01	0.0722	12.2786	0.1973E-04	0.1973E-04
23.0	0.405	0.50	0.0000	0.5262E-01	0.0758	12.9514	0.1973E-04	0.1973E-04
24.0	0.405	0.50	0.0000	0.5262E-01	0.0794	13.6344	0.1973E-04	0.1973E-04
25.0	0.405	0.50	0.0000	0.5262E-01	0.0830	14.3174	0.1973E-04	0.1973E-04
26.0	0.405	0.50	0.0000	0.5262E-01	0.0866	14.9986	0.1973E-04	0.1973E-04
27.0	0.405	0.50	0.0000	0.5262E-01	0.0902	15.6815	0.1973E-04	0.1973E-04
28.0	0.405	0.50	0.0000	0.5262E-01	0.0938	16.3645	0.1973E-04	0.1973E-04
29.0	0.405	0.50	0.0000	0.5262E-01	0.0974	17.0475	0.1973E-04	0.1973E-04
30.0	0.405	0.50	0.0000	0.5262E-01	0.1010	17.7305	0.1973E-04	0.1973E-04
31.0	0.405	0.50	0.0000	0.5262E-01	0.1046	18.4135	0.1973E-04	0.1973E-04
32.0	0.405	0.50	0.0000	0.5262E-01	0.1082	19.0965	0.1973E-04	0.1973E-04
33.0	0.405	0.50	0.0000	0.5262E-01	0.1118	19.7795	0.1973E-04	0.1973E-04
34.0	0.405	0.50	0.0000	0.5262E-01	0.1154	20.4625	0.1973E-04	0.1973E-04
35.0	0.405	0.50	0.0000	0.5262E-01	0.1190	21.1455	0.1973E-04	0.1973E-04
36.0	0.405	0.50	0.0000	0.5262E-01	0.1226	21.8285	0.1973E-04	0.1973E-04
37.0	0.405	0.50	0.0000	0.5262E-01	0.1262	22.5115	0.1973E-04	0.1973E-04
38.0	0.405	0.50	0.0000	0.5262E-01	0.1298	23.1945	0.1973E-04	0.1973E-04
39.0	0.405	0.50	0.0000	0.5262E-01	0.1334	23.8775	0.1973E-04	0.1973E-04
40.0	0.405	0.50	0.0000	0.5262E-01	0.1370	24.5605	0.1973E-04	0.1973E-04
41.0	0.405	0.50	0.0000	0.5262E-01	0.1406	25.2435	0.1973E-04	0.1973E-04
42.0	0.405	0.50	0.0000	0.5262E-01	0.1442	25.9265	0.1973E-04	0.1973E-04
43.0	0.405	0.50	0.0000	0.5262E-01	0.1478	26.6095	0.1973E-04	0.1973E-04
44.0	0.405	0.50	0.0000	0.5262E-01	0.1514	27.2925	0.1973E-04	0.1973E-04
45.0	0.405	0.50	0.0000	0.5262E-01	0.1550	27.9755	0.1973E-04	0.1973E-04
46.0	0.405	0.50	0.0000	0.5262E-01	0.1586	28.6585	0.1973E-04	0.1973E-04
47.0	0.405	0.50	0.0000	0.5262E-01	0.1622	29.3415	0.1973E-04	0.1973E-04
48.0	0.405	0.50	0.0000	0.5262E-01	0.1658	30.0245	0.1973E-04	0.1973E-04
49.0	0.405	0.50	0.0000	0.5262E-01	0.1694	30.7075	0.1973E-04	0.1973E-04
50.0	0.405	0.50	0.0000	0.5262E-01	0.1730	31.3905	0.1973E-04	0.1973E-04
51.0	0.405	0.50	0.0000	0.5262E-01	0.1766	32.0735	0.1973E-04	0.1973E-04
52.0	0.405	0.50	0.0000	0.5262E-01	0.1802	32.7565	0.1973E-04	0.1973E-04
53.0	0.405	0.50	0.0000	0.5262E-01	0.1838	33.4395	0.1973E-04	0.1973E-04
54.0	0.405	0.50	0.0000	0.5262E-01	0.1874	34.1225	0.1973E-04	0.1973E-04
55.0	0.405	0.50	0.0000	0.5262E-01	0.1910	34.7955	0.1973E-04	0.1973E-04
56.0	0.405	0.50	0.0000	0.5262E-01	0.1946	35.4785	0.1973E-04	0.1973E-04
57.0	0.405	0.50	0.0000	0.5262E-01	0.1982	36.1615	0.1973E-04	0.1973E-04
58.0	0.405	0.50	0.0000	0.5262E-01	0.2018	36.8445	0.1973E-04	0.1973E-04
59.0	0.405	0.50	0.0000	0.5262E-01	0.2054	37.5275	0.1973E-04	0.1973E-04
60.0	0.405	0.50	0.0000	0.5262E-01	0.2090	38.2105	0.1973E-04	0.1973E-04
61.0	0.405	0.50	0.0000	0.5262E-01	0.2126	38.8935	0.1973E-04	0.1973E-04
62.0	0.405	0.50	0.0000	0.5262E-01	0.2162	39.5765	0.1973E-04	0.1973E-04
63.0	0.405	0.50	0.0000	0.5262E-01	0.2198	40.2595	0.1973E-04	0.1973E-04
64.0	0.405	0.50	0.0000	0.5262E-01	0.2234	40.9425	0.1973E-04	0.1973E-04
65.0	0.405	0.50	0.0000	0.5262E-01	0.2270	41.6255	0.1973E-04	0.1973E-04
66.0	0.405	0.50	0.0000	0.5262E-01	0.2306	42.3085	0.1973E-04	0.1973E-04
67.0	0.405	0.50	0.0000	0.5262E-01	0.2342	42.9915	0.1973E-04	0.1973E-04
68.0	0.405	0.50	0.0000	0.5262E-01	0.2378	43.6745	0.1973E-04	0.1973E-04
69.0	0.405	0.50	0.0000	0.5262E-01	0.2414	44.3575	0.1973E-04	0.1973E-04
70.0	0.405	0.50	0.0000	0.5262E-01	0.2450	45.0405	0.1973E-04	0.1973E-04
71.0	0.405	0.50	0.0000	0.5262E-01	0.2486	45.7235	0.1973E-04	0.1973E-04
72.0	0.405	0.50	0.0000	0.5262E-01	0.2522	46.4065	0.1973E-04	0.1973E-04
73.0	0.405	0.50	0.0000	0.5262E-01	0.2558	47.0895	0.1973E-04	0.1973E-04
74.0	0.405	0.50	0.0000	0.5262E-01	0.2594	47.7725	0.1973E-04	0.1973E-04
75.0	0.405	0.50	0.0000	0.5262E-01	0.2630	48.4555	0.1973E-04	0.1973E-04
76.0	0.405	0.50	0.0000	0.5262E-01	0.2666	49.1385	0.1973E-04	0.1973E-04
77.0	0.405	0.50	0.0000	0.5262E-01	0.2702	49.8215	0.1973E-04	0.1973E-04
78.0	0.405	0.50	0.0000	0.5262E-01	0.2738	50.4945	0.1973E-04	0.1973E-04
79.0	0.405	0.50	0.0000	0.5262E-01	0.2774	51.1775	0.1973E-04	0.1973E-04
80.0	0.405	0.50	0.0000	0.5262E-01	0.2810	51.8605	0.1973E-04	0.1973E-04
81.0	0.405	0.50	0.0000	0.5262E-01	0.2846	52.5435	0.1973E-04	0.1973E-04
82.0	0.405	0.50	0.0000	0.5262E-01	0.2882	53.2265	0.1973E-04	0.1973E-04
83.0	0.405	0.50	0.0000	0.5262E-01	0.2918	53.9105	0.1973E-04	0.1973E-04
84.0	0.405	0.50	0.0000	0.5262E-01	0.2954	54.5935	0.1973E-04	0.1973E-04
85.0	0.405	0.50	0.0000	0.5262E-01	0.2990	55.2765	0.1973E-04	0.1973E-04

87.0	0.135	0.60	C.0000	0.6214E+04
88.0	0.140	0.70	C.0000	0.7367E+04
90.0	0.155	0.70	C.0000	0.7367E+04
91.0	0.175	0.70	C.0000	0.7367E+04
92.0	0.190	0.70	C.0000	0.7367E+04
93.0	0.200	0.70	C.0000	0.7367E+04
94.0	0.200	0.70	C.0000	0.7367E+04
95.0	0.200	0.70	C.0000	0.7367E+04
96.0	0.200	0.70	C.0000	0.7367E+04
97.0	0.200	0.70	C.0000	0.7367E+04
98.0	0.200	0.70	C.0000	0.7367E+04
99.0	0.200	0.70	C.0000	0.7367E+04
102.0	0.200	0.70	C.0000	0.7367E+04
103.0	0.200	0.70	C.0000	0.7367E+04
104.0	0.200	0.70	C.0000	0.7367E+04
105.0	0.200	0.70	C.0000	0.7367E+04
106.0	0.200	0.60	C.0000	0.6302E+04
107.0	0.200	0.60	C.0000	0.6314E+04
108.0	0.200	0.50	C.0000	0.5262E+04
109.0	0.200	0.50	C.0000	0.5262E+04
110.0	0.200	0.50	C.0000	0.5262E+04
				TOTAL O LOSS= 0.3909
				TOTAL C LOSS= 0.2470

JCB      I OVERFLOW      DATA CARDS READ      LINES PRINTED      CARDS PUNCHED      FG/TOTAL  
 STATISTICS      I      COCCCC      CCCCCC      000087      000438      GGGGG  
 COMPUTER CENTRE I.I.T. KANPUR INDIA      COMPUTER CENTRE I.I.T. KANPUR INDIA      \*\*\*  
 COMPUTER CENTRE I.I.T. KANPUR INDIA      COMPUTER CENTRE I.I.T. KANPUR INDIA      \*\*\*

PERIODIC TESTS = 95 : 0000  
SECTION TESTS = 95 : 0000  
SOLID STATE CIRCUITS = 95 : 0000  
CAPACITANCE CIRCUITS = 95 : 0000  
WEIGHT OF PLATE CIRCUITS = 95 : 0000

WATERFALLS = 60000000  
CLOUDS = 70000000  
WIND = 100000000  
WATER = 100000000

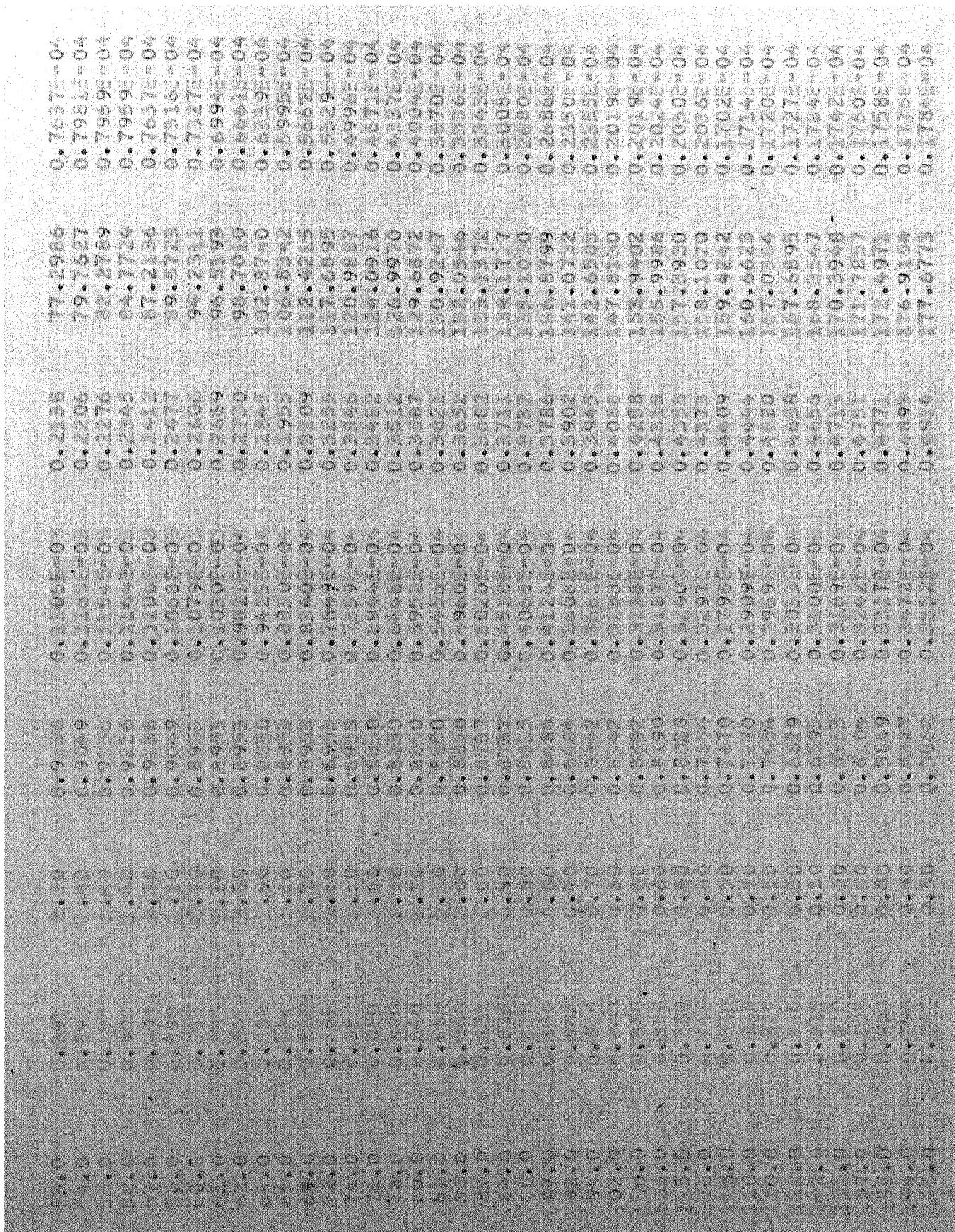


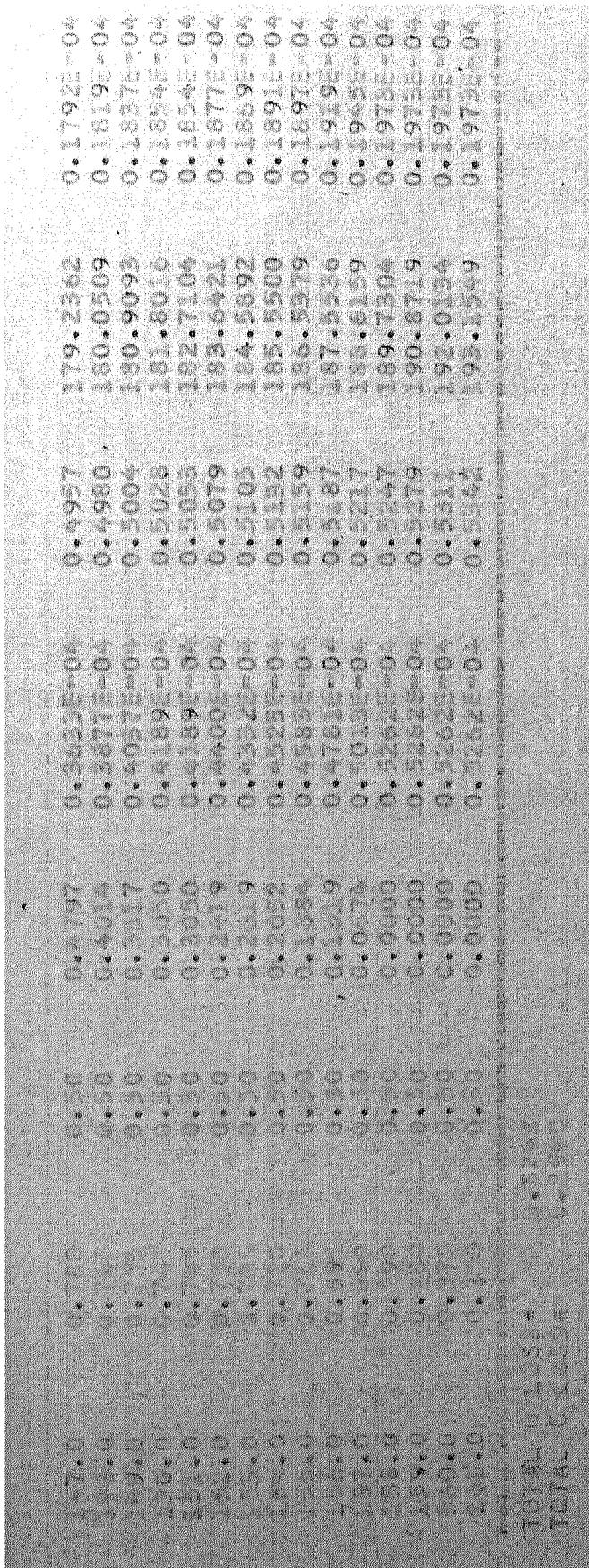
### **APPENDIX - III**

**SAMPLE COMPUTER PRINTOUTS ASSUMING  
CO-CO<sub>2</sub>-C<sub>2</sub> EQUILIBRIUM TO BE "FROZEN"  
AT REACTION TEMPERATURE.**

















\*\*\*\*\*  
JUNIOR COMPUTER CENTER  
TATI STICKS  
PUTTANAHALLI,  
INDIA-560 074  
\*\*\*\*\*





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MAY 13, 1935



## APPENDIX -IV

Tables of the results of the experiments

## Experiment No. 1

Iron ore powder + graphite

Reaction temp. =  $1047^{\circ}\text{C}$ 

Time min	Pct reduction	$\frac{\text{v}_c}{\text{gmc/gmo-sec}} \times 10^4$
2.0	5.00	3.4896
3.0	9.44	2.7509
4.0	17.84	15.4396
5.0	29.03	9.1696
7.0	46.32	7.9215
10.0	66.50	5.6546
12.0	76.60	4.1263
15.0	86.40	2.2415
19.0	93.80	1.5233
23.0	100.00	1.3900

Experiment No. 2

Iron ore powder + graphite

Reaction temperature =  $1042^{\circ}\text{C}$ .

Time min	per reduction	$\frac{V_{c,f}}{\text{gas/gene-sec}}$ $\times 10^{-4}$
2.0	5.53	4.6143
3.0	10.82	4.3022
4.0	16.14	13.5811
6.0	39.12	10.9347
7.0	47.93	9.1677
9.0	62.12	7.1769
12.0	77.63	4.6663
13.0	86.73	2.6689
19.0	93.89	1.7157
23.0	100.00	1.7670

Experiment No. 3

Iron ore powder + graphite

Reaction temperature = 1013°C

Time min	Pct reduction	$\frac{V_c}{gas/gas-sec} \times 10^4$
2.0	2.62	1.6023
7.0	15.06	1.6023
8.0	18.52	2.0009
9.0	23.69	6.6130
12.0	40.17	6.0813
16.0	57.62	4.2140
20.0	70.36	3.2046
22.0	87.64	1.6654
37.0	100.00	1.0598

Experiment No. 4

Iron ore powders graphite

Reaction temperature = 974°C

Time min	pct reduction	$\frac{w}{w_0} \times 10^4$
3.0	3.36	0.7169
9.0	10.31	0.5192
23.0	22.91	0.3708
39.0	32.77	0.4203
41.0	35.34	0.5192
45.0	41.7	0.7169
47.0	43.7	0.9147
50.0	47.2	1.2114
55.0	55.2	1.4386
61.0	64.8	1.2608
69.0	75.5	1.0136
80.0	87.2	0.7169
85.0	90.8	0.4944

Experiment No. 5

Iron ore powder + graphite

Reaction temp. =  $933^{\circ}\text{C}$

Time min	Pct reduction	$\frac{v}{e,f}$ gas/gm-sec $\times 10^4$
2.0	0.88	0.4950
12.0	5.66	0.1980
17.0	7.17	0.0990
67.0	15.6	0.0990
115.0	26.7	0.1980
185.0	41.9	0.0990

Experiment No. 6

Iron ore pellets + graphite

Reaction temp = 1054° C

Time min	Pct reduction	$\frac{w}{e,f}$ gmc/gmc-sec $\times 10^4$
2.0	2.51	2.9982
5.0	12.30	2.1453
9.0	21.10	1.7576
16.0	34.17	1.6283
27.0	51.08	1.5249
37.0	65.30	1.5249
41.0	70.72	1.4474
50.0	81.80	1.1889
62.0	92.33	0.6012
73.0	100.00	0.3102

Experiment No. 7

Iron ore pellets + graphite

Reaction temp. =  $1052^{\circ}\text{C}$

Time min	per reduction	$\frac{w}{c}$ gms/gad-sec $\times 10^4$
3.0	8.54	2.6197
5.0	16.10	2.2372
9.0	25.70	1.3911
15.0	35.10	1.2335
21.0	44.40	1.1349
31.0	57.8	1.0761
45.0	75.3	1.0761

Experiment No. 8

Iron ore pellets + graphite

Reaction temp. =  $1019^{\circ}\text{C}$

Time min	pct reduction	$\dot{w}_{e,f}$ gms/gne-sec $\times 10^4$
2.0	3.73	1.8985
3.0	6.70	1.8844
9.0	23.00	1.0325
15.0	27.60	1.1100
34.0	44.30	1.0325
46.0	70.70	1.0325
56.0	90.50	1.2132

Experiment No. 9

Iron ore pellets + graphiter  
Reaction temp. = 972°c

Time min	pet reduction	$\frac{w_e}{gms/gms, sec}$ $\times 10^4$
3.0	2.72	1.1945
8.0	6.32	0.8829
27.0	25.2	0.7531
64.0	36.7	0.7531
90.0	83.0	1.0647
97.0	90.0	0.9348
110.0	100.0	0.7531

Experiment No. 10

Pure  $\text{Fe}_2\text{O}_3$  + graphite Reaction temp. =  $935^{\circ}\text{C}$

Time min	per reduction	we $W_{C,f}$ gac/gac.sec $\times 10^4$
4.0	2.04	0.5930
16.0	12.35	0.5930
31.0	15.56	0.3365
79.0	32.27	0.3365
82.0	34.00	0.7638
84.0	35.13	1.3568
86.0	38.93	2.0359
94.0	49.68	1.6985
104.0	60.19	1.3568
119.0	71.45	0.8475
156.0	89.07	0.3365
202.0	100.00	0.2548

Experiment No. 11.

Pure  $\text{Fe}_2\text{O}_3$  graphite

Reaction temp. =  $930^{\circ}\text{C}$ .

Time min	per reduction	$\frac{w_e}{g_m \cdot sec} \times 10^4$
3.0	1.24	0.4343
27.0	11.38	0.2625
69.0	20.92	0.1730
97.0	25.00	0.0862
133.0	30.73	0.2620
135.0	31.72	0.6101
141.0	38.50	1.3164
167.0	61.79	0.6687
213.0	85.00	0.3482
234.0	100.00	0.2620

C) Interpretation of ore-graphite powder mixture and pure

$\text{Fe}_2\text{O}_3$  - graphite powder mixture:

The  $w_{c,f}$  Vs pct reduction curves for ore-graphite powder mixture (fig 6-1) and (6-2) as well as  $\text{Fe}_2\text{O}_3$  -graphite powder mix (fig 6-4) show the two stage behaviour as reported earlier by Otsuka and Kunii (fig. 1-3). The rates of the second stage are higher compared to those in the first stage. The rates do not become zero at 100 pct. reduction because of experimental errors.

Otsuka and Kunii explain this enhancement of rate in the second stage as due to catalytic effect of reduced iron on the rate of gasification reaction. A confirmation of their contention was that they found the activation energy to be high (55-75) Kcal in the first stage and low (15-23 kcal) in the second stage.

Fig 6-5 shows  $\log w_{c,f}$  Vs  $\frac{1}{T}$  plots. For ore-graphite mixture, activation energy ( $E$ ) = 105 Kcal/mole at 10 pct. reduction (first stage) and  $E$  = 70 Kcal/mole for 60 pct. reduction (second stage). Noting that the activation energy of uncatalysed gasification reaction is 80-90 Kcal/mole, the following points emerge.

1. The reaction between ore and graphite powder is controlled by the rate of gasification.
2. Catalytic enhancement of rate, presumably by reduced iron is occurring in the second stage.

Fig. 6-5 also shows that the rates in ore graphite are not substantially different from those in  $\text{Fe}_2\text{O}_3$  -graphite system.

This is expected if gasification reaction is rate controlling and therefore confirms the above conclusion no. 1.

For  $\text{Fe}_2\text{O}_3$ -graphite reaction, no attempt was made to determine the activation energy since there were data only at two temperatures.

D) Interpretation for ore-pellet-graphite powder mixtures:

This differed from the ore powder-graphite powder mixture in the following respects

1. The  $\dot{w}_{\text{C},f}$  Vs pct reduction curves show one peak at less than 10 pct. reduction. Above 30 pct reduction the rates are steady and lower. Therefore these are marked by absence of the enhancement at the second stage as in the case with the powder mixture.
2. Activation energy is lower (34-Kcal/mole for 20 pct. reduction and 17 Kcal/mole for 60 pct. reduction) compared to those with powder mixtures.
3. The rate at 60 pct reduction is substantially less compared to the same for powder mixture.
4. The rates at 20 pct reduction are less at higher temperatures but more at lower temperatures compared to those for powder mixture.

The lowering of the rate may very well be explained as due to less contact surface area in the pellet graphite case. The absence of an enhanced second stage may be due to any of the followings:

1. Gasification reaction not controlling the rate
2. The gasification reaction is controlling, but either catalyzed or uncatalyzed throughout. The uncatalyzed case is ruled out because of the low activation energy.

Lowering of the activation energy may be due to:

1. Ore reduction rate controlling
2. Gasification rate controlling, but catalyzed throughout the reduction period.
3. Long range diffusion in graphite rate controlling.

In order to clarify it further literature data on rate of reduction of iron oxides by carbon monoxide was picked up from the investigations in the past.

Bickenese and clarke (18) prepared synthetic FeO (-12 to + 16 mesh) from pure  $\text{Fe}_2\text{O}_3$  and Fe, then compacted this FeO and subjected it to reduction in CO in packed bed by the thermobalance technique. They could fit their rate data with the following equation:-

$$(1-(1-f)^{1/3})/t = (4.3 \exp(-\frac{13,800}{RT})) \times \left(\frac{C_e - C}{C_e}\right) \quad (6.11)$$

Where  $f$  = fractional reduction

$t$  = time in minutes

$C_e$  = equilibrium concentration of  $\text{CO}_2$  in equilibrium with  $\text{Fe}_x\text{O} - \text{Fe}$ .

$C$  = actual concentration of  $\text{CO}_2$  in the gas stream

Smith and McKewan (15) studied the kinetics of reduction of hematite ore pellets of 1.5 - 1.9 cm dia meter and porosity.  $\approx 0.21$  in pure CO and  $\text{CO}_2\text{-H}_2$  gas mixture by single pellet thermobalance technique. They fitted their rate equation as:

$$K = \frac{R_0 d_0 (1 - (1-f)^{1/3})}{t} \dots\dots \quad (16-12)$$

Where  $K$  = rate constant in  $\text{mg/cm}^2/\text{min}$

$R_0$  = original pellet radius

$d_0$  = oxide density

For pure CO,  $K = B \exp\left(-\frac{8500}{RT}\right)$  and values were 14.9 at  $935^\circ\text{C}$  and 18.2 at  $1038^\circ\text{C}$ .

Noting that in this investigation, pellet diameters were approximately 5 mm, porosity approximately 30 pct (assumed) and that there were 5 pellets in each experiment, some sample calculations were made as follows.

- i) Time taken to alter  $f$  from 0.4 to 0.8 was calculated from the equations of Bickness and Clark as well as Smith and McKewan. The gas was taken as pure CO.
- ii) Assuming  $\text{CO}/\text{CO}_2$  ratio to be 4:1, carbon loss rate and hence  $w_{e,f}$  were calculated.
- iii) The corresponding loss of oxygen was calculated.

Results of such calculations are presented in fig. 6-5  
It may be noted that the calculated rates are fairly close to those  
obtained from experiments. Low activation energy is also expla-  
ined. Hence it is concluded that the ore reduction stage is con-  
trolling the rate of reduction between ore pellet and graphite,  
if not fully, at least partially.

CHAPTER VIISUMMARY AND CONCLUSIONS:

- 1) Oxygen sensor was fabricated using CSZ as solid electrolyte.
- 2) Sensor performance was tested in  $O_2-N_2$  mixtures (oxygen conc. in the range 1 pct- 10 pct) and air in the temperature range of  $1050^{\circ}K - 1250^{\circ}K$ . Data obtained fall within 20 pct of those estimated from flow meter reading. In most of the cases the error was positively which indicates that the source of error may be poor electrode contact. Also at low oxygen concentration the scatter of flowmeter may be the other source of error.
- 3) Using the flowmeter and above sensor, kinetics of reduction of iron ore by carbon was investigated.-325 mesh powder and 5 mm. sintered pellets of iron ores from Rajhara mines (Durg) was used . Some experiments were also performed using pure  $Fe_2O_3$  powder. The temperature range of the experiments was  $925^{\circ}C - 1050^{\circ}C$ .
- 4) Computer calculations were executed to obtain CO fraction, pct. reduction, cumulative carbon and oxygen wt. loss, and instantaneous rates of carbon and oxygen removal.
- 5) Results indicated that the  $CO-CO_2-O_2$  equilibrium, Corresponding

to the reaction temperature remained 'frozen' even in the oxygen sensor. Therefore further calculations were done by assuming the equilibrium to be frozen. Some correction procedures were used to get the specific rate of carbon weight loss ( $\dot{W}_{c,f}$ ) and pct. reduction.

- 6) The ore powder-graphite powder mixture as well as pure  $Fe_2O_3$ , graphite mixture show two-stage behavior. Second stage show enhanced rate of reduction presumably by catalysis. Activation energy for the reaction is high. Hence gasification is concluded to be rate controlling.
- 7) The ore pellets-graphite mixtures show low activation energy and reduction rates are also lower. Assuming ore reduction stage to be rate controlling, rates of ore reduction in pure CO were calculated based on the literature information. These calculations are in good agreement with the results calculated from the experimental data. This indicates that the ore reduction step is at least partially rate controlling.

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APPENDIX V.

THEORETICAL CALCULATIONS FOR THE REDUCTION  
OF PELLETS ASSUMING REDUCTION STAGE TO BE  
RATE CONTROLLING

Weight of the ore pellets = 1 gm.

Weight of the graphite = 0.4 gm.

$$W_0 = \Delta f \times \text{Weight of oxygen in ore pellet}$$

$$= \Delta f \times 0.236$$

Consider the time interval during which fractional reduction ( $f$ ) changed from 0.8 to 0.4.

$f$	$1-f$	$(1-f)^{1/3}$	$\Delta(1-f)^{1/3}$	$\Delta W_0$ gm.
0.4	0.6	0.843		
0.8	0.2	0.565	0.236	0.113

$$\dot{W}_0 = \frac{\Delta W_0}{\Delta t} = \frac{\Delta W_0}{\Delta (1-f)^{1/3}} = \frac{\Delta(1-f)^{1/3}}{\Delta t} \quad (1)$$

$$= 0.438 \times \frac{(1-f)^{1/3}}{t}$$

Thus by knowing  $\frac{(1-f)^{1/3}}{t}$  from literature data,  $\dot{W}_0$

can be calculated.

Now assume O<sub>2</sub>/CO<sub>2</sub> ratio ( $y$ ) = 4/1

$$\text{Then, } \frac{W_C}{W_0} = \frac{12}{32} = \frac{2(y+1)}{y+2} = \frac{12}{32} = \frac{10}{6} = \frac{5}{3} \quad (2)$$

$$\text{Hence } \dot{W}_C = \frac{5}{3} \dot{W}_0$$

$$\text{It is already stated that } \dot{W}_{C,f} = \frac{\dot{W}_C}{\text{original wt. of carbon}} \quad (3)$$

1) Calculations assuming Bicknese and Clarke relationship to be valid.

$$\frac{1-(1-f)^{1/3}}{t} = 4.3 \exp\left(\frac{-13,800}{RT}\right) \times \frac{C_0 - C}{C_0}$$

Since the gas is assumed to be pure CO, C = 0.

$$\therefore \frac{C_0 - C}{C_0} = 1$$

So at the reaction temperatures, corresponding  $\frac{1-(1-f)^{1/3}}{t}$  values are known, from which  $\dot{W}_O$ ,  $\dot{W}_C$  and  $\dot{W}_{f,f}$  can be calculated.

Thus the calculated results are:

Expt. No.	Temp. °K	$\frac{\Delta(1-f)^{1/3}}{\Delta t(\text{sec}^{-1})}$	$\dot{W}_O \times 10^4$ gm/sec.	$\dot{W}_C \times 10^4$ gm/sec.	$\dot{W}_{f,f} \times 10^4$ (sec <sup>-1</sup> )
6	1327	4.10	1.80	1.125	2.812
7	1329	4.08	1.79	1.12	2.78
8	1292	3.31	1.48	0.906	2.26
9	1248	2.72	1.103	0.69	1.72

2) Calculations assuming Smith and McKewan's equation to be valid.

$$K = \frac{\pi d_o (1-(1-f)^{1/3})}{8}$$

$d_o$  = radius of the pellets = 0.25 cm.

$d_o$  = density of the pellets = 3.7 gm/cc  
(assuming 30% porosity).

Values of K are 14.9 and 18.2  $\text{mg/cm}^2/\text{min}$  at  $955^\circ\text{C}$  and  $1038^\circ\text{C}$  respectively.

From this data  $\frac{\ln(1-f)}{t}^{1/3}$  can be calculated at  $955^\circ\text{C}$  and  $1038^\circ\text{C}$  and then  $\dot{w}_0$ ,  $\dot{w}_c$  and  $\dot{w}_{e,f}$  have been obtained as shown earlier.

Thus the results obtained are :

Temp. $^\circ\text{K}$	$\frac{\ln(1-f)}{t}^{1/3}$ ( $\text{Sec}^{-1}$ )	$\dot{w}_0 \times 10^4$ $\text{cm}^2/\text{sec}$	$\dot{w}_c \times 10^4$ $\text{cm}^2/\text{sec}$	$\dot{w}_{e,f} \times 10^4$ $\text{cm}^2/\text{sec}^{-1}$
1223	2.68	1.175	0.734	1.835
1211	3.33	1.432	0.899	2.247

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